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Chemical Category

TOLUENE DIISOCYANATE (584-84-9)

INTERNATIONAL ISOCYANATE INSTITUTE, INC.

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Dear Sir or Madam:

As required by 40 CFR 716, as amended, we herewith subn..   copy of the following recently completed health and safety study.

Fate of TDI in the Atmosphere, Part II

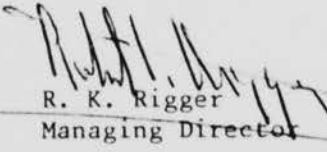| Chemical Name	CAS Number
2,4 Toluenediisocyanate	584-84-9
2,6 Toluenediisocyanate	91-08-7
Toluenediisocyaanate (isomer mixture)	26417-62-5

The III reference number 11047, has been marked on the top of the title page of the report. Please refer to this identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

This study is sponsored by the International Isocyanate Institute on behalf of the following:

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FINAL COMPILATION

FATE OF TDI, PART II

VAPOUR PHASE STUDIES

This final report comprises a draft final report plus two letters (partly manuscript), describing the additional work carried out to fulfil the contract. The contractor failed to draw together all the information into a single final report. Accordingly, it was decided to issue the three elements under the present cover page.

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Date of Compilation: 6 May 1993

III Project NA-E-24 Part II

Contractor: Battelle, Columbus Laboratories, Ohio, USA

DRAFT FINAL REPORT

on

THE FATE OF TOLUENE DIISOCYANATE
IN THE ATMOSPHERE
(PHASE II)

to

THE INTERNATIONAL ISOCYANATE
INSTITUTE

February 5, 1985

by

M. W. Holdren, C. W. Spicer, and R. M. Riggin

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, OH 43201

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DRAFT FINAL REPORT

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INTRODUCTION

In February, 1982, the International Isocyanate Institute (III) contracted with Battelle's Columbus Laboratories to investigate the atmospheric fate of toluene diisocyanate (TDI). The purpose of the study was to determine whether the gas phase reaction of TDI with water vapor is significant under atmospheric conditions and whether toluenediamine (TDA) or other potentially hazardous products are formed during the reaction. These experiments were carried out in Battelle's 17 m^3 environmental chamber. The conclusions of the study can be summarized succinctly as follows[1]:

• TDI is a highly adsorptive gas which is removed from the vapor phase by deposition on the Teflon walls of the chamber. This removal mechanism is analogous to the atmospheric process of dry deposition. The rate of removal of TDI from the gas phase by adsorption is similar to the rate observed for various other polar or low volatility compounds.

• No evidence was found for a gas phase reaction between TDI and H_2O. The rate of TDI removal was unchanged, within experimental error, for experiments in which the relative humidity was varied

from 7 to 70 per cent (TDI initial concentrations ranged from 40 to 600 ppb). Experiments in which particle formation was monitored demonstrated that less than 0.1 percent of the TDI condensed to form particles. Experiments with a total organic carbon analyzer, a chemiluminescence nitrogen-group monitor and a liquid chromatographic method specific for TDI showed that all three techniques yielded similar TDI gas phase loss rates. The results show that the organic carbon and the nitrogen moiety are removed from the gas phase at the same rate as the TDI itself, indicating physical removal from the gas phase, rather than chemical conversion.

● Two very sensitive methods, one based on liquid chromatography and one employing direct mass spectrometry/mass spectrometry, were employed to search for TDA as a possible reaction product. Conversion of TDI to TDA at a level of 0.1 percent or greater would have been detected by the liquid chromatography method. No TDA was observed with the exception of one experiment in which a trace level of TDA (0.1 percent conversion) seemed to be formed. The MS/MS method would have detected 0.4 ppb of TDA or TDI-urea, and in fact, should be capable of detecting TDA at much lower concentrations. Neither compound was observed.

The studies conducted thus far do not elucidate the reaction in condensed phase (e.g. rain drops, fog, clouds), but in the absence of liquid water droplets it seems clear that the reaction with water does not control the lifetime and fate of TDI in air. If reaction with H_2O does not exert the controlling influence over the atmospheric fate of TDI, other atmospheric removal mechanisms must be examined. These are of two types: chemical and physical. The chemical processes considered to be important in affecting the atmospheric fate of organic compounds include photolytic transformations, reaction with O_3, reaction with OH (hydroxyl radical) and reaction with other trace constituents of air. Physical mechanisms include removal by rainfall, by dry deposition and by adsorption on existing particles in the air. Of the chemical processes, photolysis and reaction with O_3 can be the dominant factors for certain species, but more frequently, reaction with hydroxyl radical controls atmospheric fate and lifetime. In the case of TDI, reaction with an ubiquitous trace constituent, NH_3, may also be important.

In an effort to identify the dominant chemical or physical process which controls TDI lifetime and fate in the atmosphere, Battelle has recently carried out a series of scoping experiments in the 17.3 m^3 environmental chamber to assess the importance of the following:

- TDI photolytic decomposition

- Reaction of TDI with photochemically induced pollutants (e.g. O_3, OH radicals)

- TDI reaction with ammonia

- TDI reaction with triethylene diamine (DABCO)

- TDI adsorption on ammonium sulphate particles.

During these experiments TDI concentration was monitored using both a liquid chromatography technique and a continuous analyzer which makes use of a chemically impregnated tape. TDA product concentrations were determined by liquid chromatography.

The TDI formulation "TD-80" was used throughout the experimental program. This mixture contained 80 percent 2,4 toluene diisocyanate and 20 percent 2,6 toluene diisocyanate. Although these isomers can be distinguished by liquid chromatography (LC), all LC data are reported as a summation of the two components for comparison with the results from the continuous analyzer.

EXPERIMENTAL

A 17.3 m^3 indoor environmental chamber, with a surface to volume ratio of 2.5 m^{-1}, was used to study the reaction of TD-80. The chamber is constructed of aluminum but is presently lined with Teflon film (fluorinated ethylene polymer i.e. FEP). Ultra-high purity air (total non-methane hydrocarbon content $\leq$ 0.01 ppmC) was continually supplied to the chamber for dilution and purging operations by an Aadco clean air generator.

For irradiation experiments the chamber was operated with a light intensity (k_1) of 0.20 min^{-1} as determined by NO_2 photolysis. This intensity was achieved through the use of 96 blacklights and 15 sunlamps interspersed throughout the lampbank. The spectral distribution of the sunlamps peaks in intensity at a wavelength of about 310 µm. Peak intensity for the blacklamps occurs near 370 µm.

The operating temperature of the chamber was controlled by a combination of heating or cooling the surrounding laboratory air and external heat lamps mounted on the top of the chamber. Humidity was regulated by an external humidifier which circulated the chamber air over a hot water bath until the desired humidity was obtained.

The chamber contained a heated recirculating manifold for precision injection of liquids, and a series of manifolded flowmeters for gas injection. A hot plate mounted inside the chamber was utilized for vaporizing TD-80 and triethylene diamine. The plate temperature was controlled by a variac. A variable speed stainless steel fan is provided for mixing the chamber contents. Numerous sampling ports extend into the chamber for gas and aerosol monitoring instrumentation.

Instrumentation

The analytical instrumentation employed during the chamber study is listed in Table 1. TDI was monitored with a continuous analyzer using a chemically impregnated tape and was also determined every 30 to 45 minutes using impinger/liquid chromatography procedures. TDA was measured by LC methods with the same impinger samples used for TDI collection. Detailed C_2-C_{10} hydrocarbon measurements were made every thirty minutes. Peroxyacetyl nitrate and sulfur hexafluoride determinations were made every fifteen minutes. Aerosol number concentration and size distribution were made several times during each experiment. Light scattering coefficient was determined with the integrating nephelometer once the ozone concentration had peaked. Ozone, nitrogen, oxides, total hydrocarbons, temperature and humidity were monitored continuously.

TABLE 1. ANALYTICAL INSTRUMENTATION EMPLOYED DURING CHAMBER STUDY

Variable	Method	Instrumentation
Toluene diisocyanate	Liquid chromatography/ UV detector	Laboratory Data Control Model 1203 detector
Toluene diisocyanate	Chemically impregnated tape	MDA Scientific 7100 Analyzer
Toluenediamine	Liquid chromatography/ electrochemical detector	Bioanalytical Systems Model LC-2A detector
Ozone	Chemiluminescence	Bendix 8002 Analyzer
Nitrogen oxides	Chemiluminescence	Monitor Labs 8440 Analyzer
Peroxyacetyl nitrate	Gas chromatography/ electron capture detection	Shimadzu-Mini 2 GC
Sulfur hexafluoride	Gas chromatography/ electron capture detection	Hewlett Packard 5970 GC
Total hydrocarbons	Continuous flame ionization detection	Beckman 402 Analyzer
Individual hydrocarbons	Gas chromatography/ flame ionization detection	Hewlett Packard 5880 GC
Aerosol		
(a) particle number concentration/size distribution	Light scattering by HeNe laser	Particle Measurement Systems Inc. ASAS Analyzer
(b) Light scattering coefficient/visual distance	Light scattering by xenon flashlamp	Meteorology Research Inc. (Model 1550) integrating nephelometer
Temperature/humidity	Chilled mirror/dew point condensation	EG&G (Model 911) hygrometer

Procedures

Chamber Operation

Prior to each experiment, the chamber was thoroughly purged with hydrocarbon free air and adjusted to the designated temperature and humidity conditions. Meanwhile each instrument was calibrated and then connected to the chamber to obtain background sampling data. All the continuous sampling equipment remained connected to the chamber throughout the entire run. As a result, the chamber was continually diluted with clean air during an actual run. The dilution rate depended primarily upon the sampling flow requirements of the analytical equipment connected to the chamber during each particular run. To determine chamber dilution during each experiment, an inert gas, sulfur hexafluoride, was injected into the chamber to obtain a nominal concentration of 6 ppb. Following the injection of SF_6, an automated gas chromatographic system was used to analyze the chamber air every fifteen minutes throughout the course of the experiment.

Chamber Loading

Chemical compounds were introduced into the chamber in the order shown in Table 2. A measured amount of the liquid TC-80 (20 µl) was placed onto a watch glass and immediately inserted inside the chamber onto a hot plate. The plate temperature was then ramped from 25° to 200°C (10 minutes). During this heating cycle, the chamber's mixing fan was turned on to accelerate sample equilibration. Injection of DABCO (triethylene diamine) in experiment 5 also required the use of the hot plate. A 0.16 gram sample was weighed on a watch glass and then immediately transferred to the chamber's hot plate. The plate temperature was slowly increased to 150°C. Complete volatilization resulted in 10 minutes. For experiments 3 through 6, measured volumes of gaseous mixtures of O_3 and NO_2 were injected to give the targeted concentrations listed in Table 2. Likewise for experiments 3 through 6, measured amounts of a standard hydrocarbon mixture containing seventeen organic species were

TABLE 2. MATRIX OF CHAMBER EXPERIMENTS FOR TDI PROGRAM[a]

Experiment	Light Conditions	Chamber Contents ($@$ 60% RH, 28°C)
1	Dark	Clean air 0.2 ppm TD-80
2	Light	Clean air 0.2 ppm TD-80
3	Light	Clean air 0.2 ppm NO_2 4.0 ppmC (HC-mix) 0.2 ppm TD-80 0.1 ppm O_3
4	Light	Same as Run 3 but with 0.5 ppm NH_3 added
5	Light	Same as Run 3 but with 2.0 ppm triethylene diamine (DABCO)
6	Light	Same as Run 3 but with ~100 μg/m^3 (NH_4SO_4) added

(a) Chamber dilution was determined during each experiment by following the disappearance of injected SF_6 (6 ppb) using gas chromatography-electron capture detection.

injected. These species and percent composition are listed in Table 3. A 9 cc injection of pure ammonia vapor gave a chamber loading of 0.5 ppm compound for experiment 4.

Ammonium sulfate aerosol was generated with a nebulizer for experiment 6. Nebulization of an $(NH_4)_2SO_4/H_2O$ solution (1 gm/ml) was performed at a rate of 0.3 ml/minute using an air flow rate of 1 l/min. through the solution. A dilution flow of 20 l/min. through the transfer tube minimized condensation of the generated aerosol. Characterization of the size range of the ammonium sulfate aerosol was carried out with the ASAS analyzer. This unit also provided a measure of particle concentration from which mass concentrations could be estimated.

Liquid Chromatography Sampling and
Analysis of TDI/TDA

Two methods were used to collect TDI samples for liquid chromatography analysis. The first method was employed to collect vapor phase TDI and utilized midget glass impingers (25 ml) containing a derivatizing reagent of N-(4-nitrobenzyl)-N-n-propylamine hydrochloride (NBPA) in toluene[2]. The second method was designed for the collection of total vapor phase and aerosol phase TDI and involved the use of glass fiber filters impregnated with the NBPA reagent.

The derivatizing solution used in the impinger method was prepared by placing 120 milligrams of NBPA in a four ounce bottle and adding 10 mL of distilled water and 13 mL of 1 $\underline{N}$ sodium hydroxide. The solution was transferred into a 60 mL separatory funnel and extracted with two mL aliquots of reagent grade toluene. The combined toluene extracts were placed in a clean four ounce bottle containing 1.5 grams of anhydrous sodium sulfate, briefly shaken, and filtered through Whatman No. 41 paper into a 250 mL volumetric flask. The filter was rinsed with 5 mL of toluene (into the volumetric flask) and the solution was diluted to 250 mL with toluene (2×10^{-3} $\underline{M}$). This stock solution was then diluted ten fold with toluene to yield a 2×10^{-4} $\underline{M}$ working solution which was used for all sample collections. All NBPA solutions were stored in Teflon-sealed brown glass bottles and refrigerated when not in use.

TABLE 3. COMPOSITION OF URBAN SURROGATE
HYDROCARBON MIXTURE

Compound	Relative Molar Concentration
Acetylene	.136
Ethane	.100
Propane	.040
2-Methylpropane	.023
n-Butane	.099
2-Methylbutane	.070
n-Pentane	.037
2-Methylpentane	.044
Ethylene	.162
Propylene	.035
Trans-2-butene	.043
2-Methylbutene-2	.013
Benzene	.029
Toluene	.061
m-Xylene	.069
p-Ethyltoluene	.025
1,2,4-trimethylbenzene	.013

The impregnated filters were obtained from Mobay Chemical Company in pre-assembled Millipore Swinnex cassettes. Each cassette was wrapped with black insulation tape to minimize exposure to light. Upon arrival at Battelle the cassettes were placed in a dessicator and refrigerated. Details on the preparation of the filters may be obtained elsewhere[3].

At least five impinger samples were collected during each experiment. A volume of ten milliliters working solution was used for sample collection. Each sample was collected at a rate of two liters per minute over a ten minute period to yield a total sampled volume of 20 liters of air.

In addition to impinger samples, impregnated filters were also collected during experiments 3 through 6. During these collections the filter cassette was either connected in series with the impinger or inserted into the sampling system in place of the impinger.

Figure 1 shows a diagram of the two collection devices connected in series. In those instances in which the filter cassette replaced the impinger, the luer-lok tube fitting was connected directly to the chamber via the 1/4" Teflon union. A pump and dry test meter were used in the sampling system to accurately measure the volume of air sampled. The rotameter provided a visual indication of flow. The valve was employed to adjust the flow.

Collected samples were processed as follows. The NBPA solution from each impinger was transferred to a 20 ml vial and placed into a heating unit (Pierce Reacti-Therm Heating Module - Model 18780). The samples were heated to 50°C and evaporated to dryness under a nitrogen flow (~200 cc/min). The residue was then dissolved in 500 µl of acetonitrile. Each filter sample was transferred to a 20 ml vial containing 10 ml of the working solution. Each vial was sonicated for several minutes and then taken to dryness and redissolved in 500 µl of acetonitrile. All samples were analyzed by HPLC using the following chromatographic conditions:

Mobile Phase -- 50/50 Acetonitrile/H_2O (50 µL of concentrated phosphoric acid per liter of water)

Column -- (5 µm) Spherisorb ODS, 25 cm x 4.6 mm
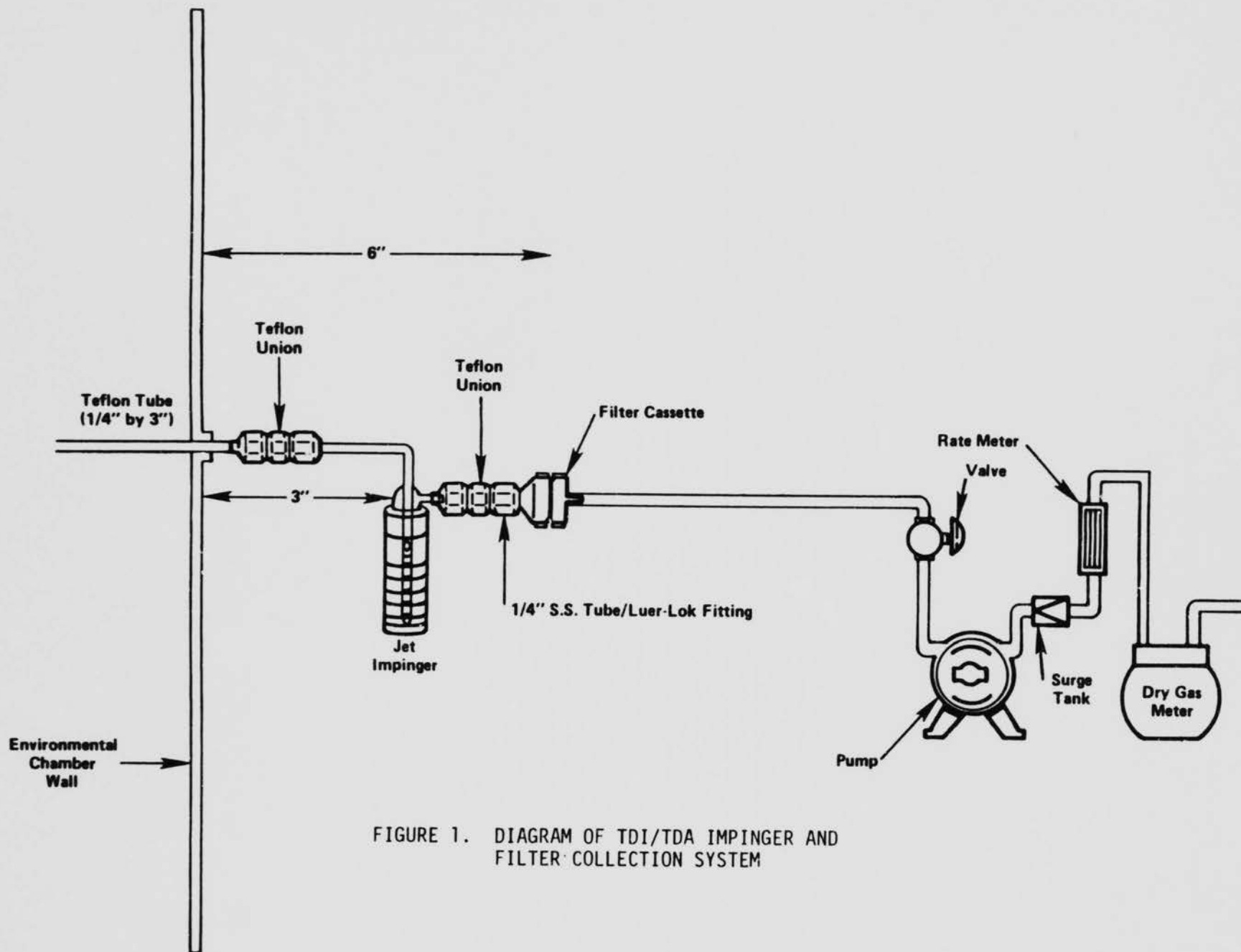
FIGURE 1. DIAGRAM OF TDI/TDA IMPINGER AND FILTER COLLECTION SYSTEM

Flow Rate -- 2 mL/minute

Detector -- UV at 254 nm

Injection Volume -- 10 μL

TDA concentrations were determined using the same sample collection and processing as for TDI. Prior to the analysis of each sample, 100 μl of the acetonitrile solution used for TDI determination was diluted with 100 μl of 0.2 M (pH 4.7) sodium acetate buffer.

This solution was analyzed for 2,4- and 2,6-TDA using the following chromatographic conditions:

Mobile Phase -- 10/90 Acetonitrile/0.2 M sodium acetate
    buffer (pH 4.7)

Column -- (5 μm) Lichrosorb RP-2, 25 cm x 4.6 mm

Flow Rate -- 1 mL/minute

Detector -- Electrochemical at 0.8 volts vs. Ag/AgCl

Injection Volume -- 50 μL

Liquid Chromatography Calibration of TDI/TDA

Fresh TDI calibration standards were prepared prior to each experiment. Measured amounts of 5, 10, and 20 μl of a stock TDI solution (1.2 μg/μl in toluene) were placed into vials containing 10 ml of NBPA working solution. These vials were then treated in a similar fashion as actual samples. A 10 μl injection of each standard corresponded to 0.12, 0.24 and 0.48 μg TDI on-column. Figure 2 shows a chromatogram of the 0.24 μg standard. The TDI formulation "TD-80" was used for all calibrations and was assumed to contain 80 percent 2,4-TDI and 20 percent 2,6-TDI isomer.

The 2,4 and 2,6 TDA isomers were dissolved in methanol solution (1 mg/ml) and diluted on a daily basis to a concentration of 20 ng/ml using the acetonitrile/acetate buffer mobile phase. The diluted standard was analyzed directly. Figure 3 shows a chromatogram for a 20 ng/ml standard of 2,6-toluenediamine and 2,4-toluenediamine.
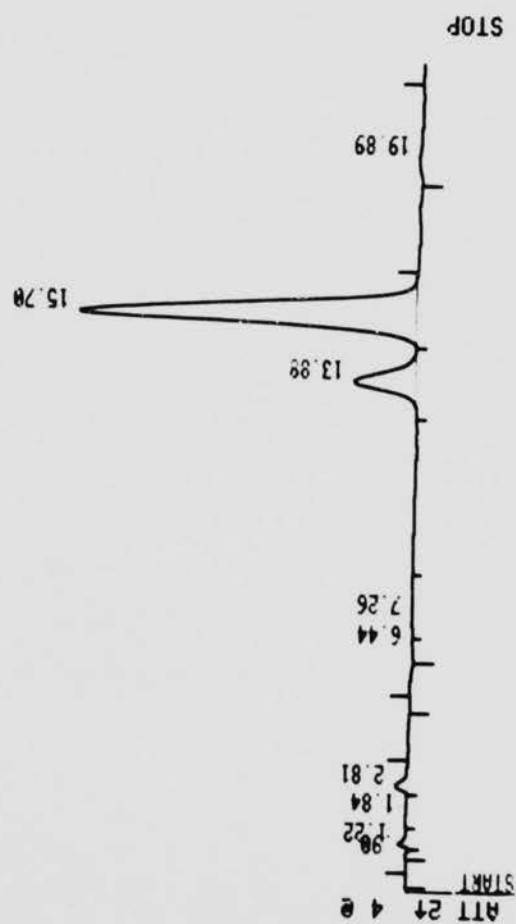
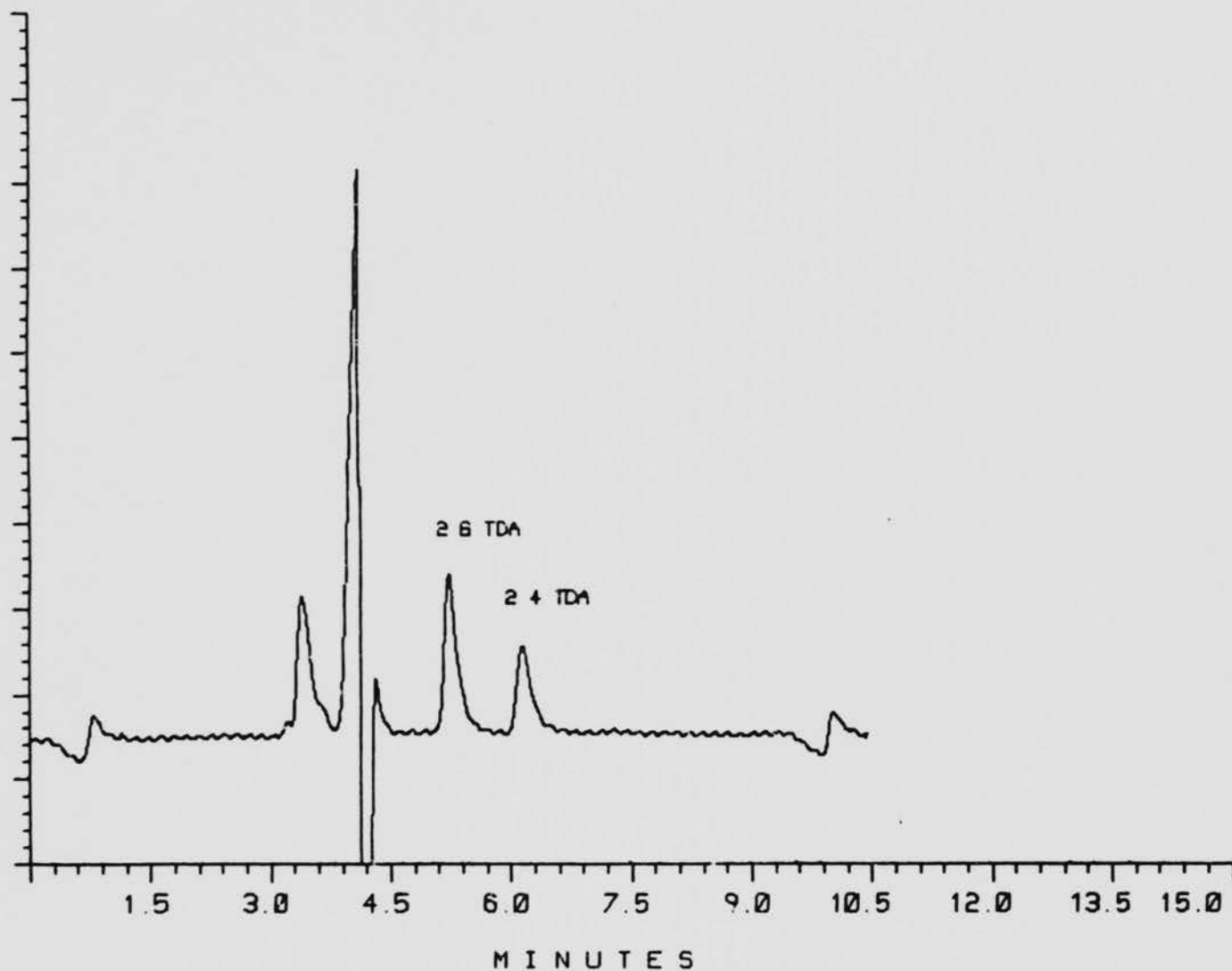FIGURE 2. CHROMATOGRAM REPRESENTING 0.24 MICROGRAMS OF TD-80 ON THE COLUMN

FIGURE 3. CHROMATOGRAM REPRESENTING 1.0 NANOGRAMS OF
2,6-TOLUENEDIAMINE AND 2,4-TOLUENEDIAMINE
ON THE COLUMN

RESULTS AND DISCUSSION

Rationale for Chamber Experiments

During the Phase II study, six chamber experiments were conducted to investigate the chemical and physical processes considered to be important in affecting the atmospheric fate and lifetime of toluene diisocyanate. These experiments are listed in Table 2. Experiment 1 was carried out to provide a baseline for comparing with Phase I results, which were also conducted under similar chamber conditions and contents. Experiment 2 provided an indication of the importance of direct photolytic decomposition. In experiments 3 through 6, the strategy was to introduce TDI into reactive polluted air, in much the same manner as TDI emissions from a plant are injected into the air. Under such circumstances the nature of the "polluted" air is expected to be very important with regard to TDI reactions. In experiment 3, the effect of hydroxyl radicals, in combination with ozone, water vapor and sunlight was examined. A hydrocarbon mixture was used to simulate the distribution of hydrocarbons found in urban environments; this same mixture has been utilized for this purpose in other chamber programs[4,5]. Ozone and nitrogen dioxide concentrations used in this experiment are typical of values observed in many urban areas. Experiment 4 was carried out with the same chamber contents described for experiment 3 but with 0.5 ppm ammonia also added. This concentration of ammonia represents at least a 25 fold increase over typical urban levels of this pollutant. Excess NH_3 was introduced into the chamber in order to identify direct gas phase reactions between TDI (200 ppb) and NH_3 (500 ppb), and also to obtain product information to levels 1 percent of initial reactant. In experiment 5 triethylene diamine (DABCO) was injected, along with TDI, in the reactive polluted air mixture listed in experiment 3. The DABCO concentration used in the experiment was suggested by III based upon typical stack emission ratios of 10/1 (DABCO/TDI). Due to the strongly adsorptive nature of TDI, experiment 6 was proposed to test the hypothesis that heterogeneous reaction between gas phase TDI and aerosol particles may serve as a significant

removal process. Sulfate aerosol was chosen because it is the dominant component of light scattering in most urban areas and has been shown to be the major contributor to aerosol mass in the 0.1 t .0 ;m size range[6-8].

TDI Method Comparison

The TDI concentrations versus irradiation time are shown in Table 4. Each experiment is listed, along with the irradiation times and corresponding TDI concentrations for the two primary sampling methods. Experiment 1 was conducted in the dark, and therefore the starting time corresponds to the time when all the reactants were injected and thoroughly mixed. Experiment 2 is actually a continuation of experiment 1. In this case the UV lights were turned on 3.95 hours after experiment 1 was initiated. In the remaining experiments, the UV lights were turned on immediately after the chamber contents were mixed.

During each experiment at least five impinger samples were collected and analyzed by liquid chromatography. A continuous monitor from MDA Scientific provided real time TDI concentrations. For comparison with the impinger samples, ten minute average values from this analyzer are reported in Table 4. For 30 percent of the samples, an impregnated filter was positioned downstream of the impinger to trap any TDI aerosol that might pass through the impinger solution. These backup filter results are shown together with the impinger data in Table 4.

The data in Table 4 demonstrate that the TDI concentrations reported by the continuous MDA analyzer and the impinger method agree very well for most of the experiments. The ratios of concentrations reported by the impinger method and the MDA analyzer are plotted versus experiment number in Figure 4. A mean ratio of .90 $\pm$ .13 was obtained for all the data points (excluding outlier in experiment 2). This mean value indicates that the overall impinger results are 10 percent lower than the continuous analyzer data. In four of the six experiments the ratio was very close to 1.0, which would indicate perfect agreement. However, the ratios for experiments 3 and 5 were significantly lower than 1.0. No change in the ratios with time was observed in either

TABLE 4. TDI CONCENTRATIONS VERSUS IRRADIATION TIME
USING VARIOUS SAMPLING TECHNIQUES

Experiment No.	Irrad. Time (hours)(a)	TDI Concentration, ppb		
		Continuous Monitor (MDA 7100)	Integrated Samples	
			Impinger	Backup Filter
1	1.10	151	141	
	1.55	135	130	
	2.13	124	116	
	2.70	111	105	
	3.23	97	92	
2	3.95	82	81	
	4.40	67	68	
	5.05	51	53	
	5.75	36	40	
	7.10	17	25	
3	0.07	184	167	
	0.42	174	138	4
	1.35	114	90	
	1.85	106	73	<2
	2.72	74	50	
	3.58	51	36	
4	0.30	172	153	
	0.85	137	136	
	1.57	102	95	<2
	2.00	88	81	
	2.70	65	65	<2
	3.67	46	48	
5	0.13	110	89	
	0.55	71	51	
	1.05	41	29	<2
	1.50	27	19	<2
	1.98	17	12	<2
6	0.25	148	149	
	0.48	128	127	
	0.98	100	96	4
	1.45	81	81	3
	2.55	51	54	<2

(a) At time zero, UV lights turned on. Note that experiment 1 was run with no UV light.
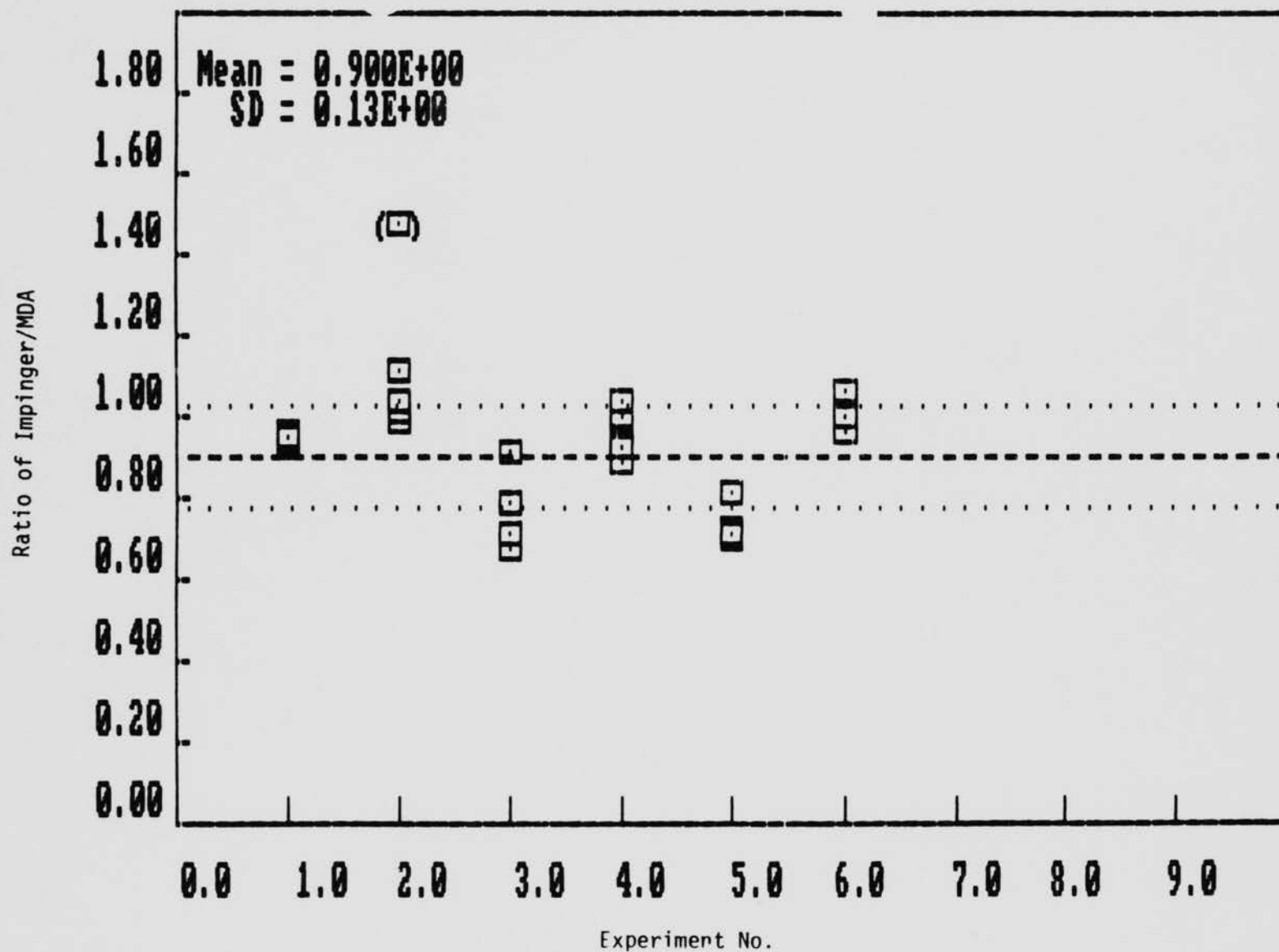In this case, time zero occurs when all reactants are mixed.

FIGURE 4. CONCENTRATION RATIOS FROM THE IMPINGER METHOD AND
THE MDA CONTINUOUS ANALYZER DURING THE SIX EXPERIMENTS

experiment. The low ratios suggest that a calibration or flow problem may have caused a shift in the concentration data reported by one of the methods, although a careful review of the records from these two experiments has failed to reveal the cause of the shift.

One question of interest is the physical state of the TDI. It is not possible to determine the extent of particle-bound TDI unambiguously from the available data, but if particle-bound TDI is inefficiently collected by impingers, as reported for particle-bound MDI[3], then the impinger/ (impinger + impregnated filter) ratios from Table 3 indicate that less than 3 percent of the TDI was present as an aerosol. This is consistent with the results of our earlier study[1]. However, if the impingers do collect particle-bound TDI, then we are unable to determine the distribution of TDI between the particle and vapor phase.

Another aspect of TDI sampling concerns the use of impregnated filters as an alternative to impingers for total TDI collection. During experiments 3 through 6, ten direct impregnated filter samples were collected along with the impinger/backup filter samples noted in Table 4. Table 5 shows the fraction of total TDI collected by direct filter sampling. The two filters used in experiment 3 were placed in nitroreagent immediately after sampling and shaken for five minutes. The apparent collection efficiency of the filters averaged 55 percent using this procedure. The remaining filters were extracted by sonication in an attempt to improve recovery of material from the filter. The apparent average collection efficiency of the seven sonicated filter samples was 84 ± 6 percent. The effect of sample flow on filter collection efficiency was examined in experiment 4 by collecting one filter at a flow of 1 l/min. Because of the lower apparent efficiency at this flow, the remaining filters were collected at the higher flow of 2 l/min.

The low collection efficiency of the filters compared to the impingers may be due to surface adsorption of TDI onto the filter holder and other connecting fittings. This explanation is consistent with the lower recoveries at lower flow rates (i.e. longer contact times). Further investigation of these issues was beyond the scope of this contract.

TABLE 5. APPARENT COLLECTION EFFICIENCY OF
TDI USING FILTER COLLECTION DEVICE

Experiment No.	Irrad. Time (hours)	Apparent Collection Efficiency, % (filter/impinger)
3	0.65	58[a]
	2.08	52[a]
4	1.08	91[b]
	2.22	69[c]
5	0.78	76[b]
	1.28	88[b]
	1.73	87[b]
6	0.72	84[b]
	1.22	87[b]
	1.68	77[b]

Average of (b) values = 84 $\pm$ 6%

(a) Filters placed in nitroreagent and shaken (5 min).

(b) Filters placed in nitroreagent and sonicated (5 min).

(c) This filter sampled with flow of 1 l/min -- remaining filters sampled with flow of 2 l/min.

TDI Kinetics

The loss rate of TDI during the chamber experiments followed first order decay behavior where $C_t = C_0 e^{-bt}$. C_t is the TDI concentration at time (t), C_0 is the initial TDI concentration at time (o) and b is the first order decay constant for TDI. Exponential curve fitting techniques were applied to the impinger and MDA data to obtain loss rate information[1]. Excellent fit of the data to the first order rate law was observed for all six experiments. Plots of the data for both methods are contained in Appendix A. The loss rate for each method has been corrected for chamber dilution (5 $\pm$ 0.1 percent/hr) and is displayed in Table 6. An average TDI loss rate and standard deviation for each experiment is also given.

Results from experiment 1 indicate a TDI loss rate of 15 percent/hr, which is very close to the average value of 18 $\pm$ 2 percent/hr found during similar experiments in the Phase I study. Irradiation of TDI in experiment 2 increased the loss rate to a value of 36 percent/hr. The use of a simulated urban air mixture (experiment 3) did not appreciably enhance the rate of disappearance of TDI when compared to the clean air irradiation experiment. The addition of NH_3 (experiment 4) and $(NH_4)_2SO_4$ aerosol (experiment 6) to the simulated urban air mixture also did not appear to significantly increase the TDI loss rate. However the addition of triethylene diamine (experiment 5) accelerated the TDI loss rate from 36 percent/hr to 99 percent/hr.

Taken at face value, the higher loss rate for experiment 2 would suggest direct photolysis of TDI was occurring. However, even though experiment 2 was conducted in "clean" air, there may have been sufficient radicals generated by trace contaminants in the air during irradiation to account for the more rapid TDI loss rate. This possibility is strengthened by the ozone and PAN data for this experiment (Appendix A). Appreciable levels of PAN and ozone (which are formed by reactions involving free radicals) were generated during irradiation, suggesting that free radical attack on TDI may have occurred. In order to distinguish between photolysis and radical reactions, the photolysis experiment should be

TABLE 6. SUMMARY OF TDI LOSS RATES DURING
CHAMBER EXPERIMENTS

	Rate of TDI Loss by Method[a] (percent/hr)		
Experiment No.	MDA	Impinger	$\bar{x}$(SD)[b]
1	15	15	15(0)
2	40	32	36(5.7)
3	32	39	36(5.0)
4	34	31	33(2.1)
5	96	102	99(4.2)
6	41	38	40(2.1)

(a) Rate has been corrected for chamber dilution of 5%/hr.

(b) $\bar{x}$ = mean value, SD = standard deviation.

repeated using a radical scavenger such as NO to suppress the effect of radical reactions.

The hydrocarbon reactants used in experiments 3 through 6 show interesting decay profiles. Table 7 shows TDI loss rates together with decay rates for five of the organic reactants present in the 17 component urban mixture. For each compound, a mean loss rate and percent standard deviation was calculated using the individual values from experiments 3,4, and 6. Reasonable standard deviations were obtained and ranged from 5 percent for m-xylene to 15 percent for ethylene. Toluene diisocyanate gave a value of 10 percent. The relatively invarient loss rates suggest that the presence of NH_3 (experiment 4) and $(NH_4)_2SO_4$ (experiment 6) do not affect the hydrocarbon degradation reactions that are taking place in the three experiments. However, a significant reduction in photochemical activity has occurred in experiment 5, as evidenced by the much lower loss rates for the five organic compounds. Decreased photochemical activity is also apparent from the ozone and PAN data in Appendix A. In experiment 5 a maximum of 30 ppb ozone and 15 ppb PAN were formed after -3 hours of irradiation. In experiments 3,4, and 6, ozone maximums ranged between 270 and 310 ppb, while maximum PAN concentrations were between 130 and 150 ppb. The presence of triethylene diamine is the likely cause of the lower reaction rate. Certain amines have been shown to be strong inhibitors of photochemical air pollution due to their radical scavenging properties[9,10]. The enhanced TDI loss rate in experiment 5 indicates that a reaction between triethylenediamine and TDI is occurring. This reaction may be taking place either in the gas phase or heterogeneously between gas phase TDI and aerosol phase triethylene diamine. Aerosol phase triethylene diamine was formed immediately following the injection of the compound into the chamber. On a quantitative basis, this aerosol amount represents only a few percent of the total triethylene diamine in the chamber. However, because the particles are submicron in size, there is a very large surface area available for reaction, and a heterogeneous component of the reaction can not be ruled out.

TABLE 7.   COMPARISON OF LOSS RATES (percent/hr)
OF TOLUENE DIISOCYANATE WITH SELECT ORGANICS
FROM THE SEVENTEEN COMPONENT MIXTURE

| | Experiment No. | | | | |
Compound	3	4	5	6	$\bar{x}$ (% SD)[a]
Ethylene	17	22	10	23	21(15)
Propene	93	119	24	106	106(12)
Toluene	7	8	7	7	7.3(8)
m-Xylene	30	28	19	27	28(5)
1,2,4-Trimethylbenzene	49	40	27	43	44(10)
Toluene diisocyanate	36	33	99	40	36(10)

(a) Means and percent standard deviations calculated from
experiments 3,4 and 6.

Search for Toluenediamine

The kinetic data in the irradiation experiments (2 through 6) indicate an enhanced loss rate of TDI compared to the non-irradiation run. To determine if toluenediamine (TDA) was formed in these experiments, a select number of impingers and filters were analyzed for the amine compound. These data are shown in Table 8. TDA was not observed above the analytical detection limit of 10 ng/ml in any of the samples. This amount of TDA corresponds to ≤ 0.1 ppb in the chamber. Based upon an initial TDI concentration of 200 ppb, a conversion of TDI to TDA at a level of 0.05 percent or greater would have been detected by the HPLC method.

SUMMARY

In an effort to identify the dominant chemical or physical processes which control TDI lifetime and fate in the atmosphere, a series of experiments have been completed. An assessment of the following processes was made:

- TDI photolytic decomposition

- Reaction of TDI with photochemically induced pollutants (e.g. O_3 OH radicals)

- TDI reaction with ammonia

- TDI reaction with triethylene diamine

- TDI adsorption on ammonium sulphate particles.

The experimental results indicated that the irradiation of TDI in "clean air" produced an increased loss rate over that observed in clean air in the dark. The use of highly polluted air did not appreciably enhance the rate of TDI disappearace compared to the clean air irradiation experiment. Experiments involving the addition of NH_3 and $(NH_4)_2SO_4$ aerosol also did not show significantly higher TDI loss rates. However, the addition of 2 ppm triethylene diamine, which is often coemitted with TDI, accelerated the TDI loss rate from 36%/hr to 99%/hr.

TABLE 8. TOLUENEDIAMINE RESULTS FOR IMPINGER AND FILTER SAMPLES

	Concentration, ng/ml	
Sample	2,6 TDA	2,4 TDA
Experiment 2		
Impinger 6	<6	<10
Experiment 3		
Impinger 6	<6	<10
Experiment 4		
Impinger 3	<6	<10
Backup Filter 3	<6	<10
Filter Alone 3	<6	<10
Impinger 4	<6	<10
Backup Filter 4	<6	<10
Filter Alone 4	<6	<10
Impinger 5	<6	<10
Experiment 6		
Impinger 3	<6	<10
Backup Filter 3	<6	<10
Filter Alone 3	<6	<10
Impinger 4	<6	<10
Backup Filter 4	<6	<10
Filter Alone 4	<6	<10
Impinger 5	<6	<10

Two analytical methods were employed for the determination of TDI concentrations during the above experiments. An impinger/liquid chromatography procedure was used to collect time-integrated samples while a continuous monitor from MDA Scientific provided real time TDI concentrations. Excellent agreement was obtained when comparing these two methods. A mean ratio of .90 ± .13 was obtained for the TDI concentrations from the impinger and the continuous analyzer. The TDI loss rates measured by the two techniques agreed within 7.5 percent (RSD) when averaged over the six experiments.

A liquid chromatographic procedure was also used to search for toluenediamine as a possible reaction product. Conversion of TDI to TDA at a level of 0.05 percent or greater would have been detected by the LC method. No TDA was observed in any of the experiments.

RECOMMENDATIONS

The clean air irradiation experiment is somewhat ambiguous, in that the enhanced TDI loss rate could be due to direct photolysis or to reaction with radicals generated by photolysis of contaminants. We suggest repeating the photolysis experiment using a radical scavenger such as NO to suppress the effect of radical reactions, in order to distinguish between the direct photolysis of TDI and free radical attack on TDI. If radical reactions appear important, then we should pursue kinetic studies of OH radical reaction with TDI. If photolysis is found to be important, an absorption spectrum of TDI is needed to confirm this pathway. Integration of the absorption spectrum over available solar wavelengths will enable us to calculate a photolysis rate constant. This rate constant will allow us to calculate the atmospheric lifetime of TDI with respect to direct photolysis.

We also envision that experiments are needed to assess the significance of the triethylene diamine (DABCO)/TDI reaction under realistic emission conditions. Initial assessment would involve obtaining the following:

- typical stack concentrations of TDI and DABCO

- ambient concentrations if available

- stack parameters--flow, height, temperature, etc.

- information on gas phase reaction of TDI/DABCO.

If ensuing calculations indicate that atmospheric DABCO/TDI reactions are important, then we should study the rate of reaction (vary concentrations) and identify reaction products.

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APPENDIX A

The following six figures show plots of TDI concentration versus time for the six experiments (data from Table 3 in text). The top plot in each figure illustrates the data from the impinger-liquid chromatography method. The lower plot depicts the data from the continuous analyzer. R^2 values are given, along with intercept (a) and slope (b) values. The intercept corresponds to the initial TDI concentration at time zero, while the slope is equivalent to the TDI loss rate plus chamber dilution.
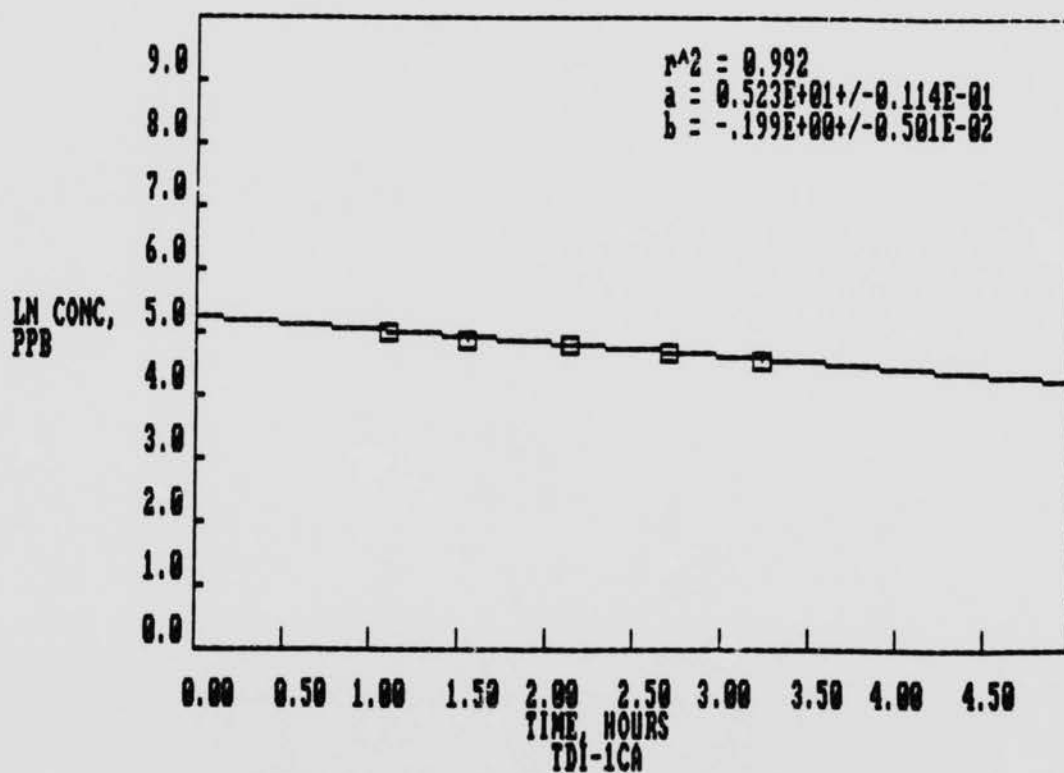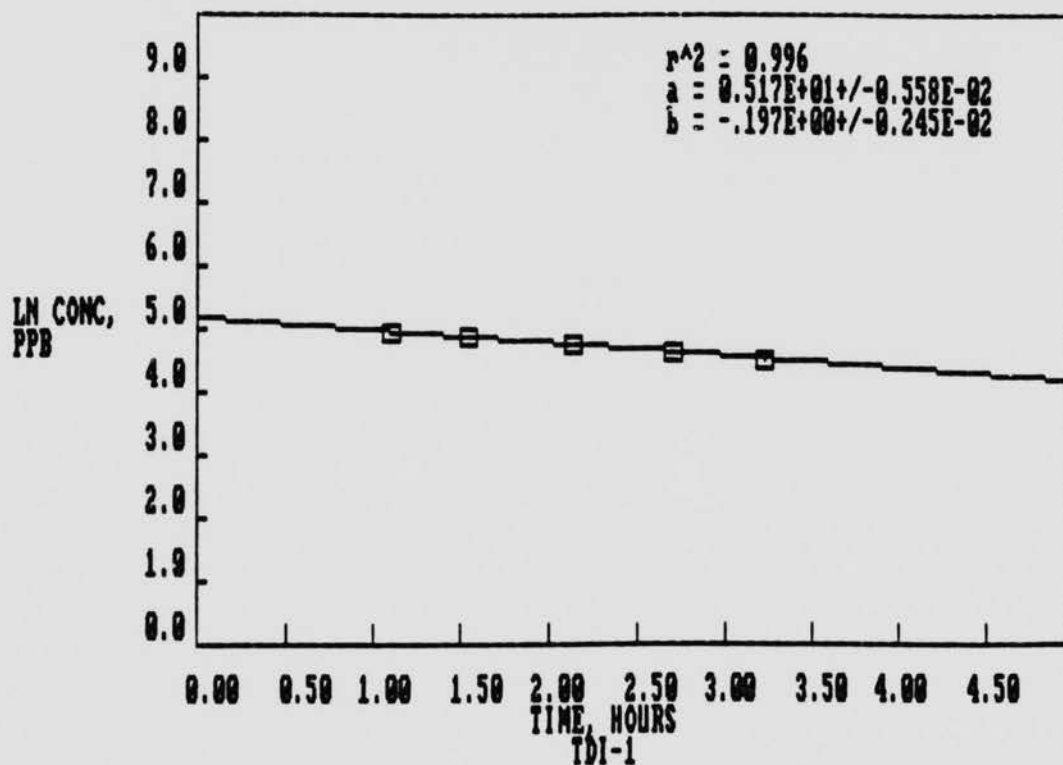
r^2 = 0.996
a = 0.517E+01+/-0.558E-02
b = -.197E+00+/-0.245E-02

LN CONC, PPB

TIME, HOURS
TDI-1

r^2 = 0.992
a = 0.523E+01+/-0.114E-01
b = -.199E+00+/-0.501E-02

LN CONC, PPB

TIME, HOURS
TDI-1CA

FIGURE A1. EXPERIMENT 1 (Clean Air--No Irradiation)
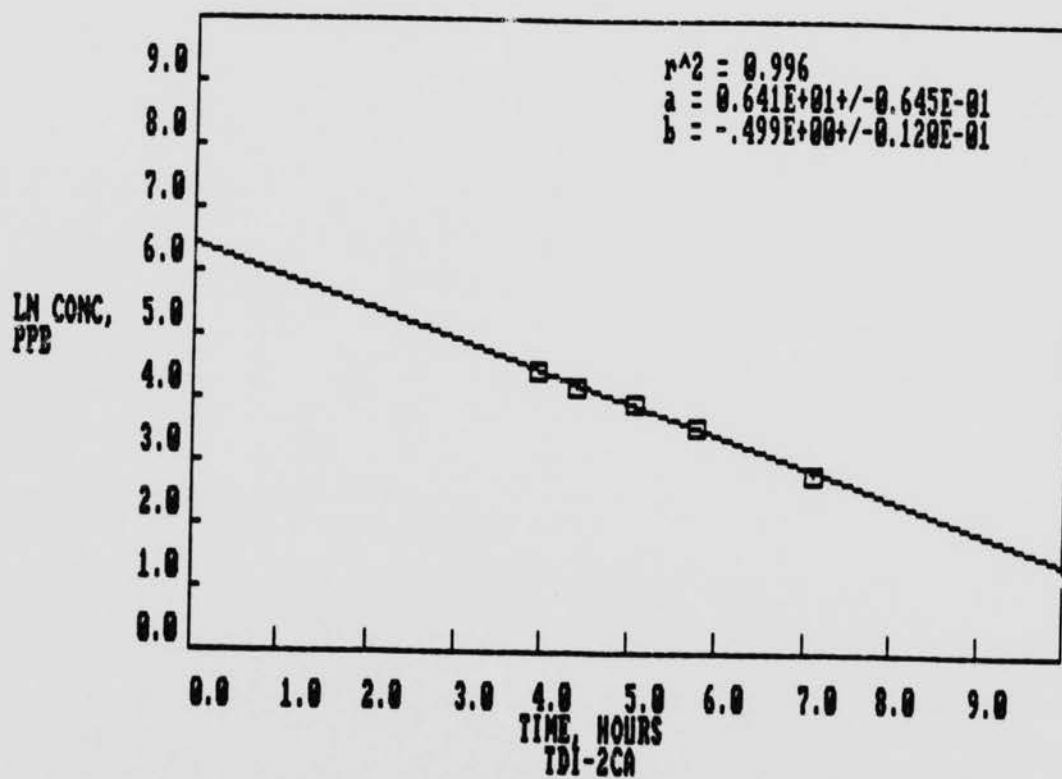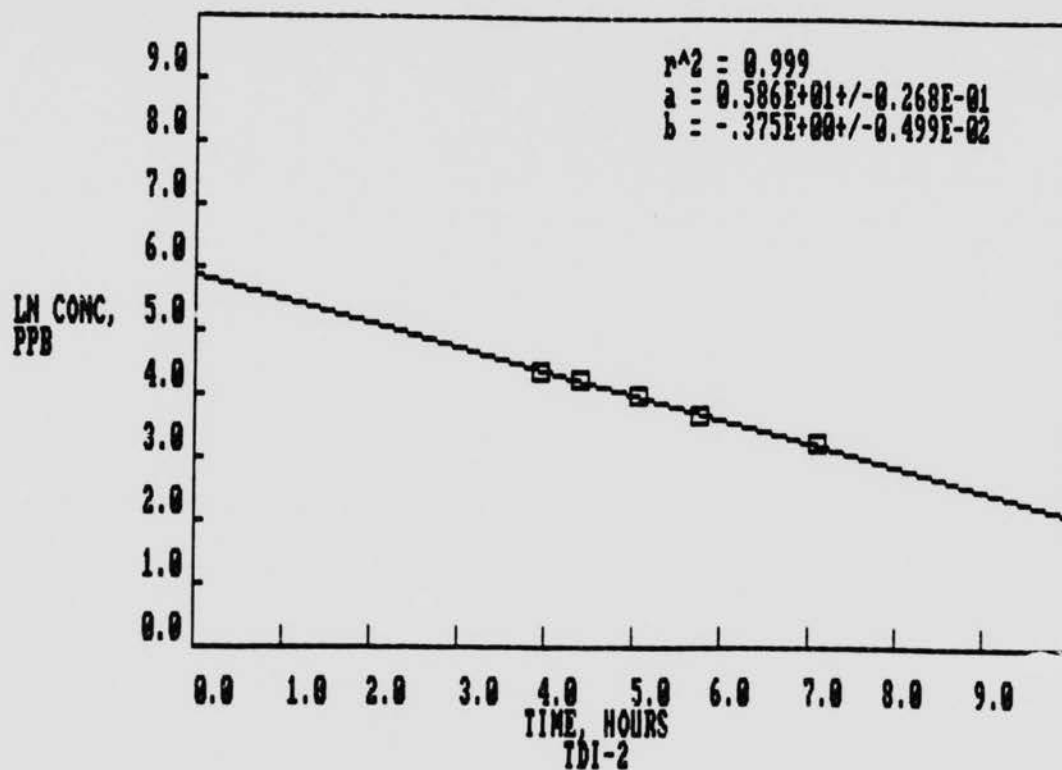
FIGURE A2.   EXPERIMENT 2 (Clean Air--Irradiation)
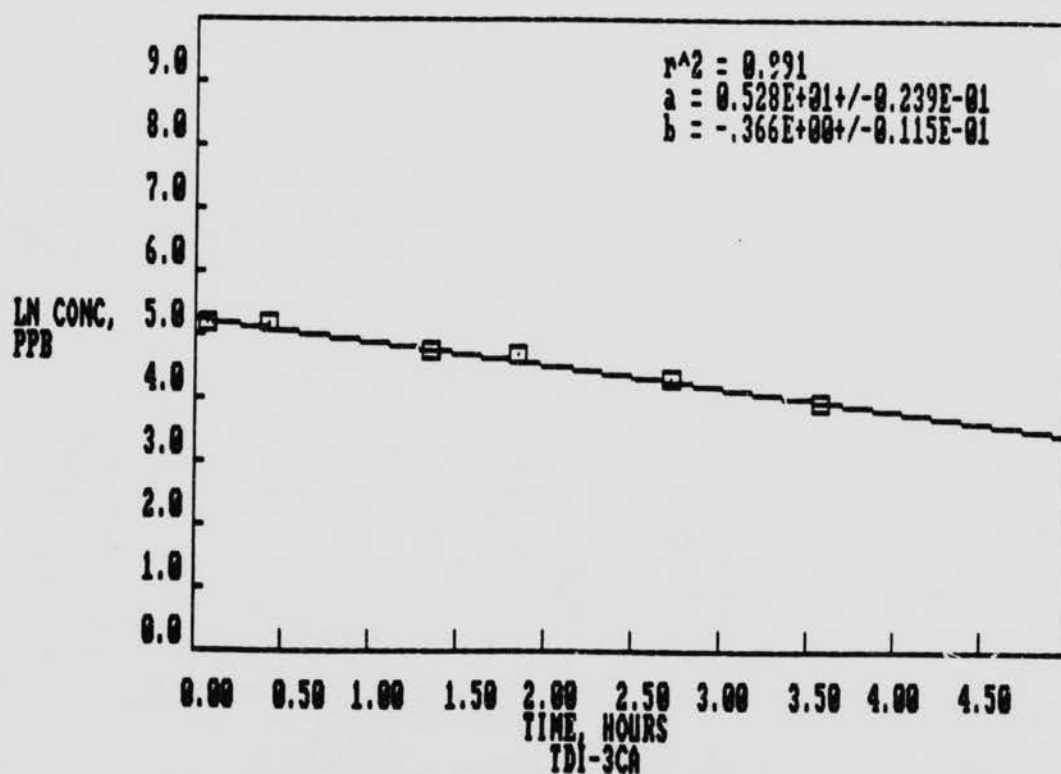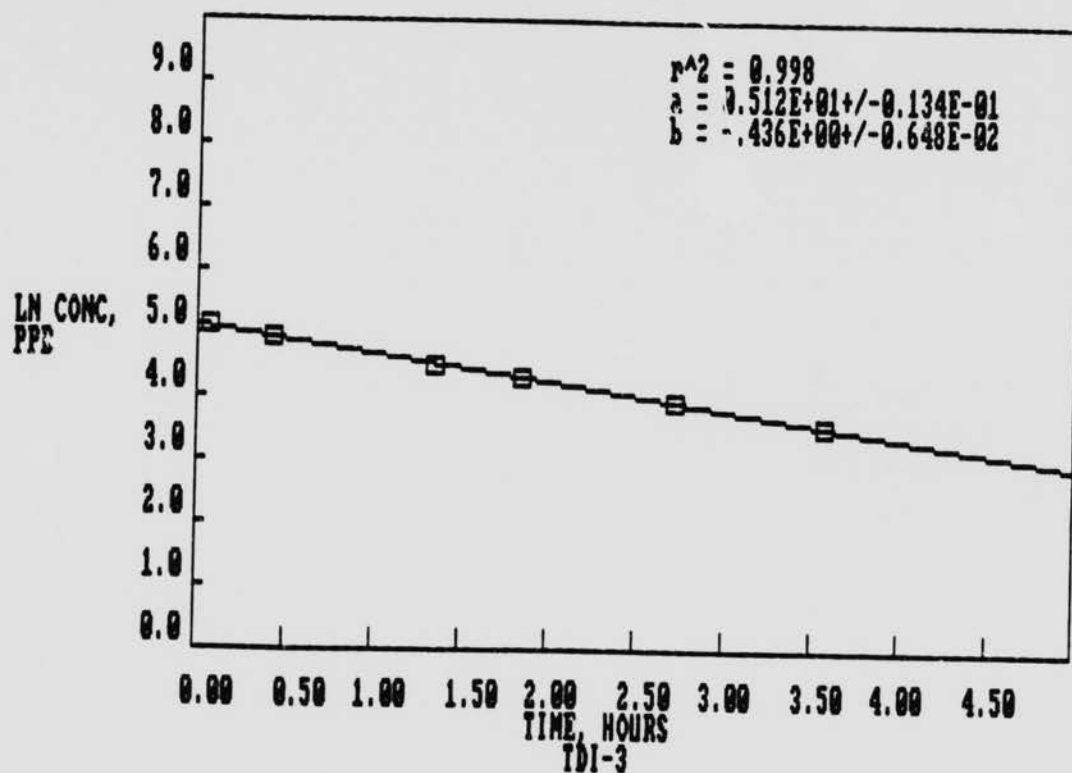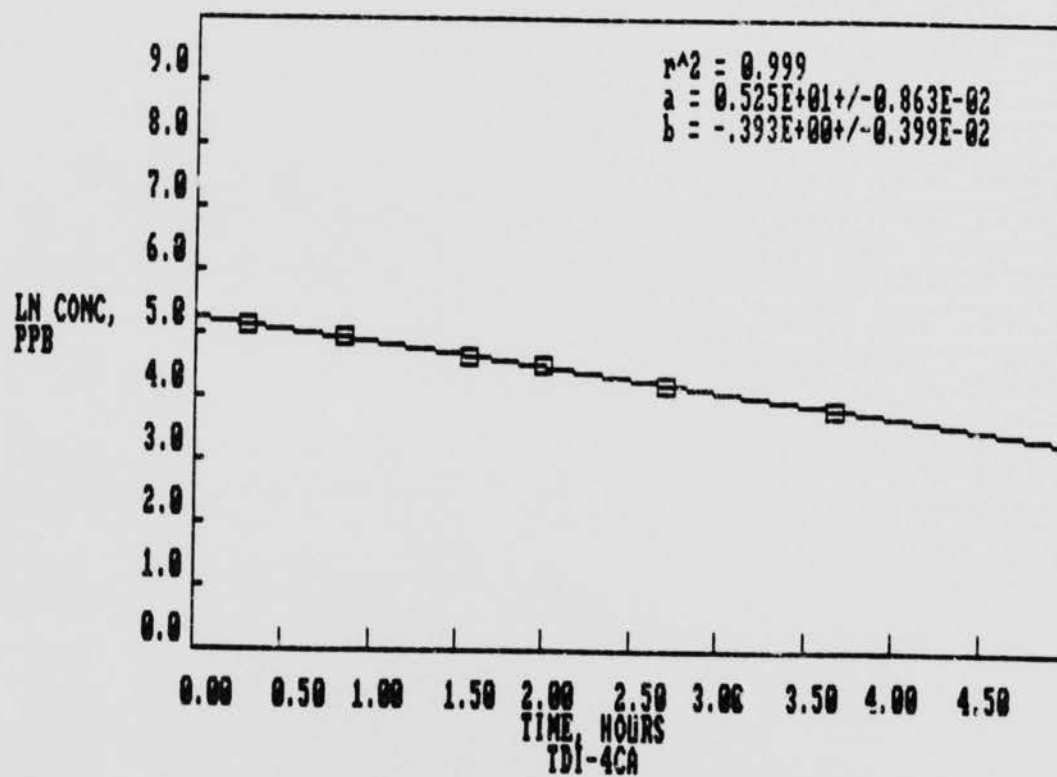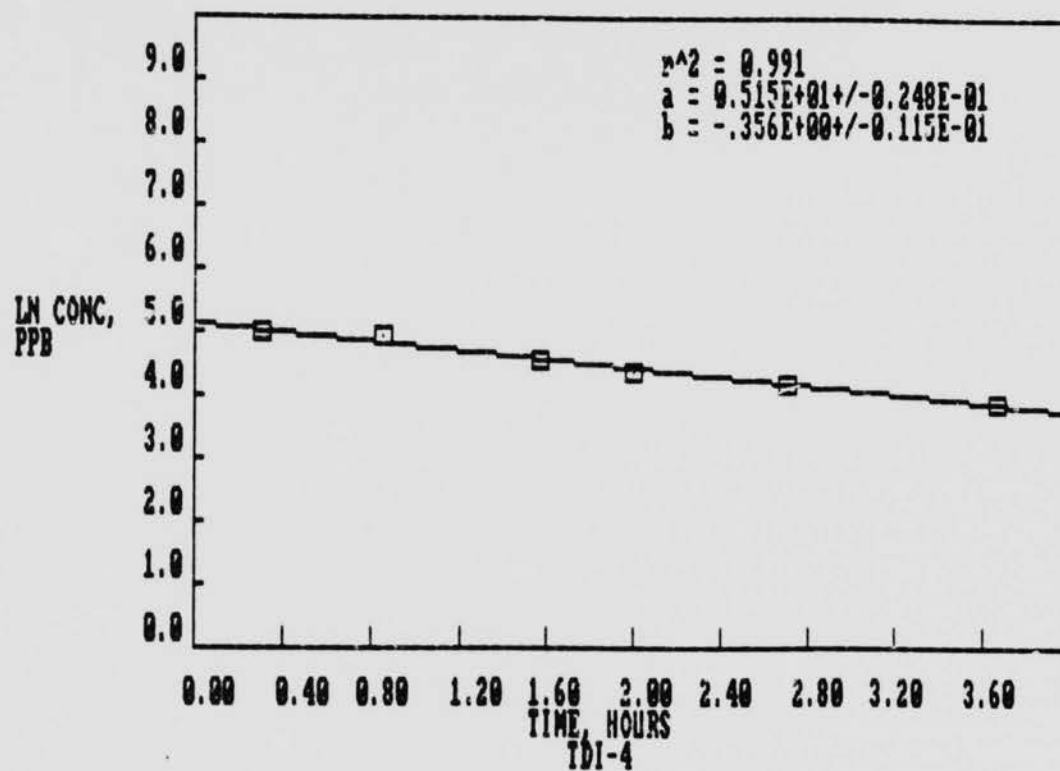
FIGURE A3.   EXPERIMENT 3 (Surrogate Urban Mixture)
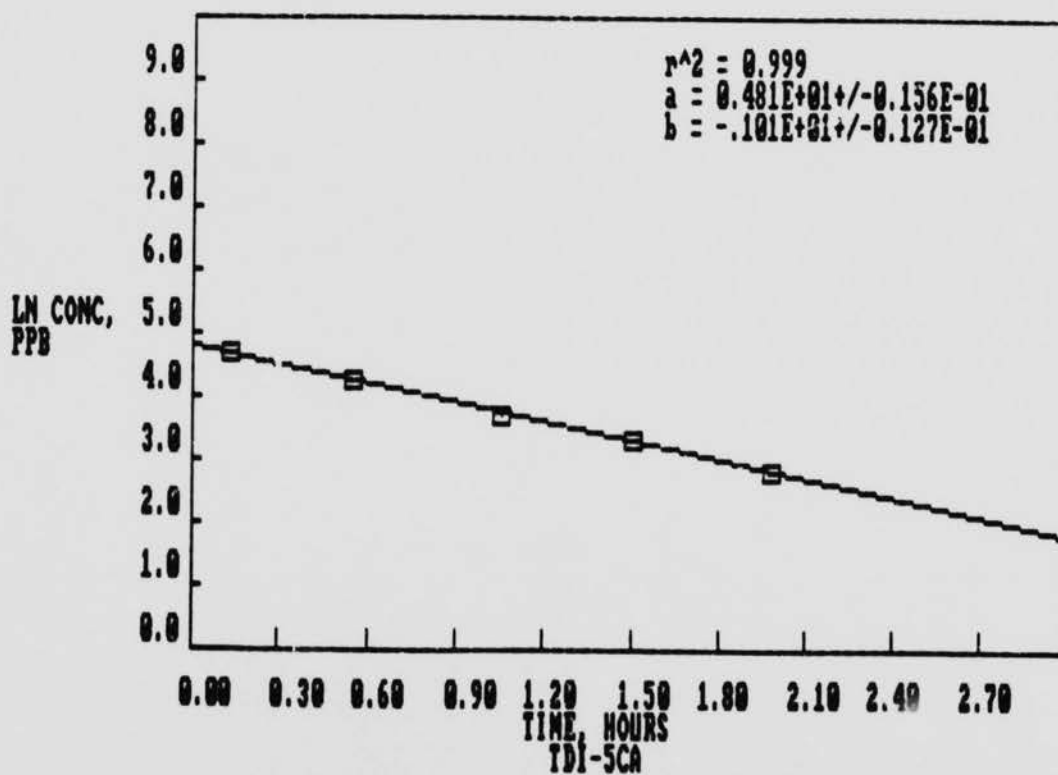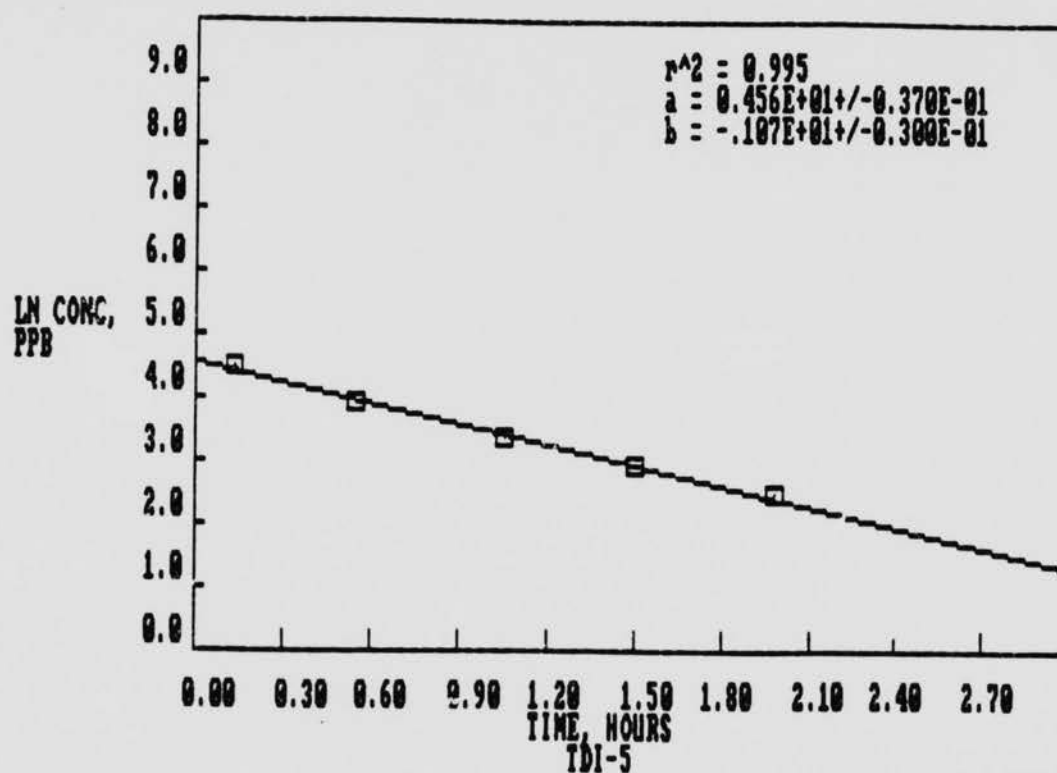
FIGURE A4.   EXPERIMENT 4 (Addition of Ammonia)

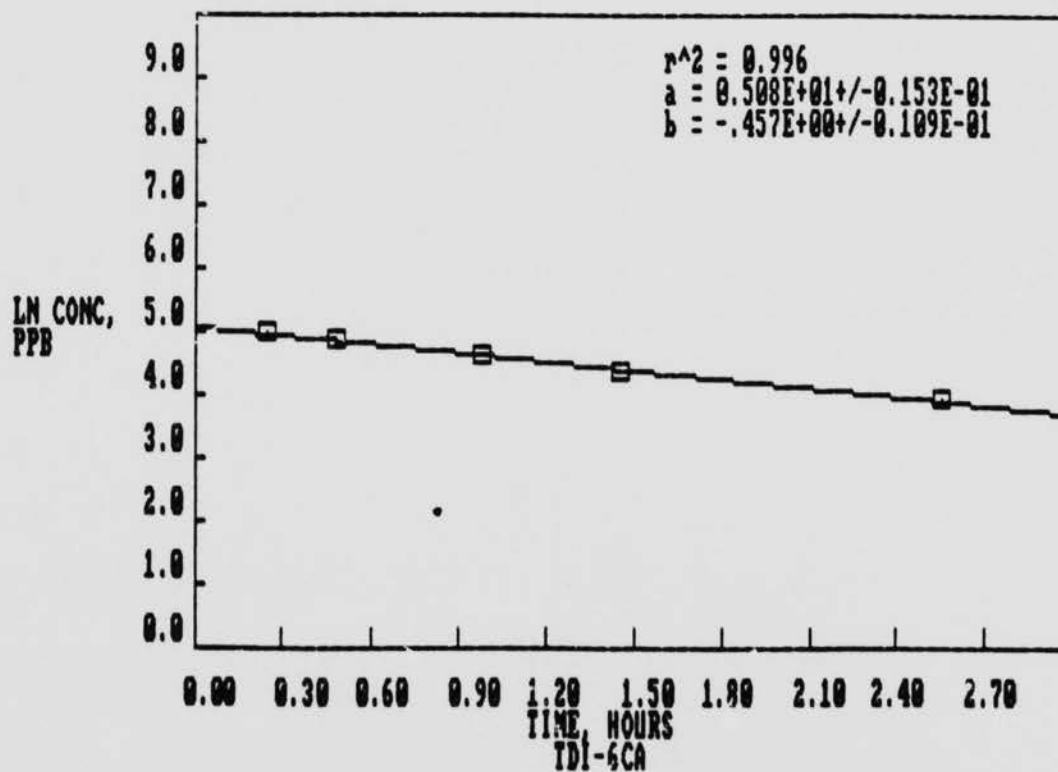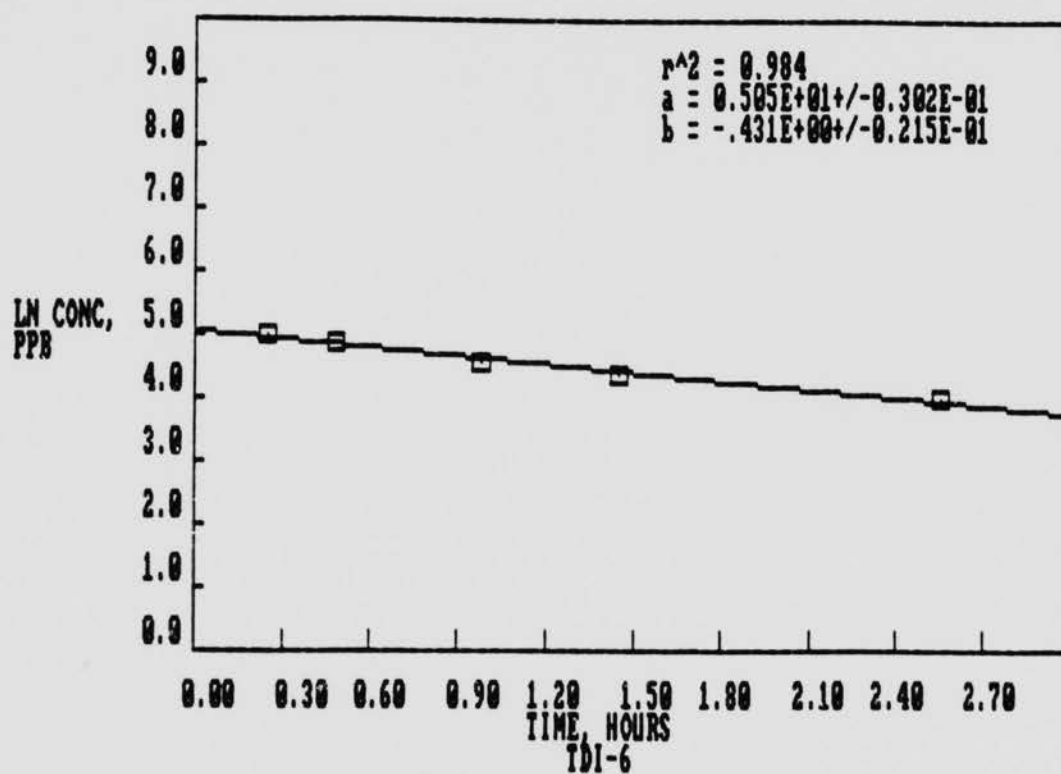FIGURE A5. EXPERIMENT 5 (Addition of DABCO)

FIGURE A6.   EXPERIMENT 6 (Addition of Ammonium Sulfate)

The following figures show the ozone, peroxyacetyl nitrate and oxides of nitrogen data during the six experiments. Visual distance as measured by the integrating nephelometer is also listed.
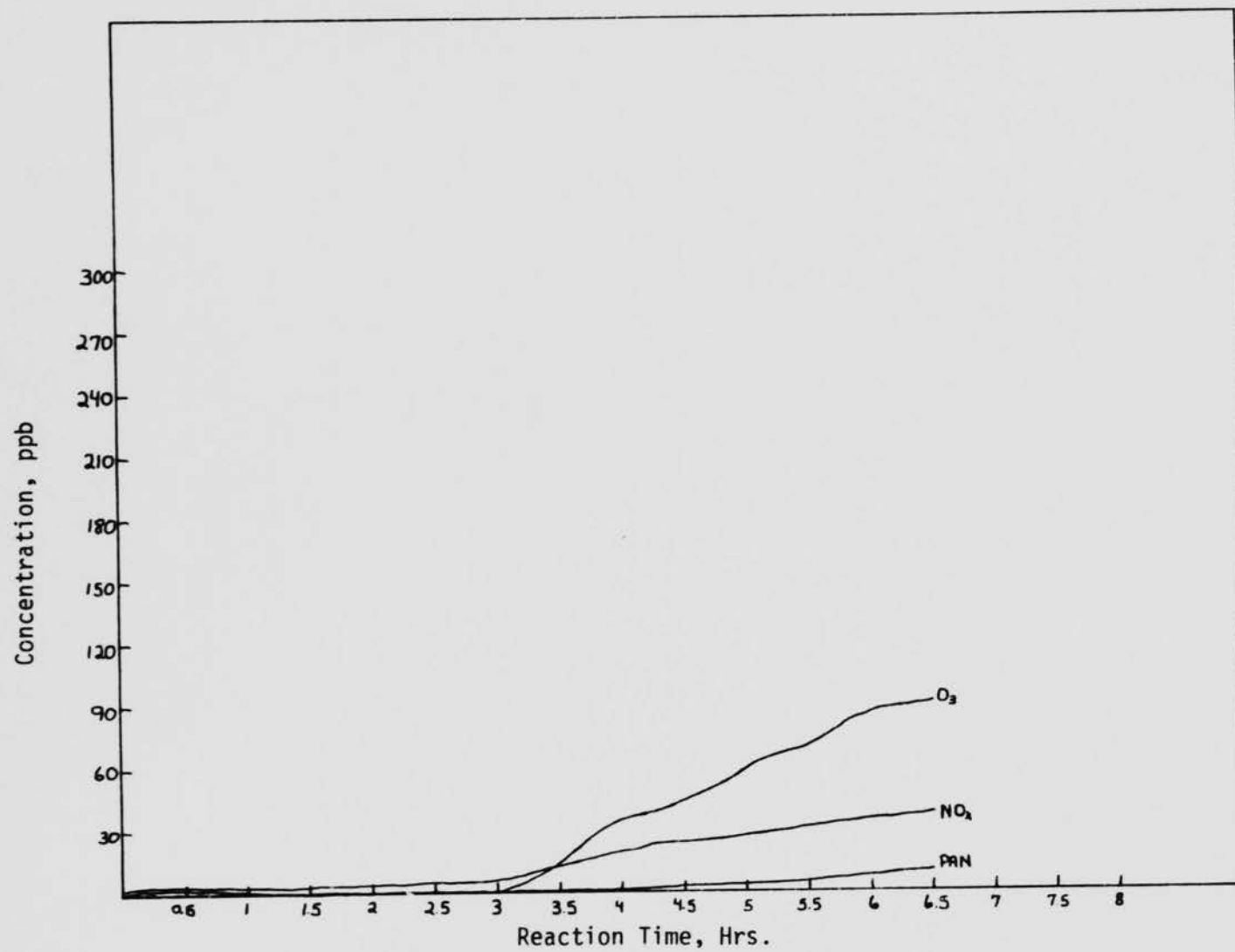
FIGURE A7. EXPERIMENTS 1 AND 2 (Visual Distance 10 Miles @ O_3 Maximum)
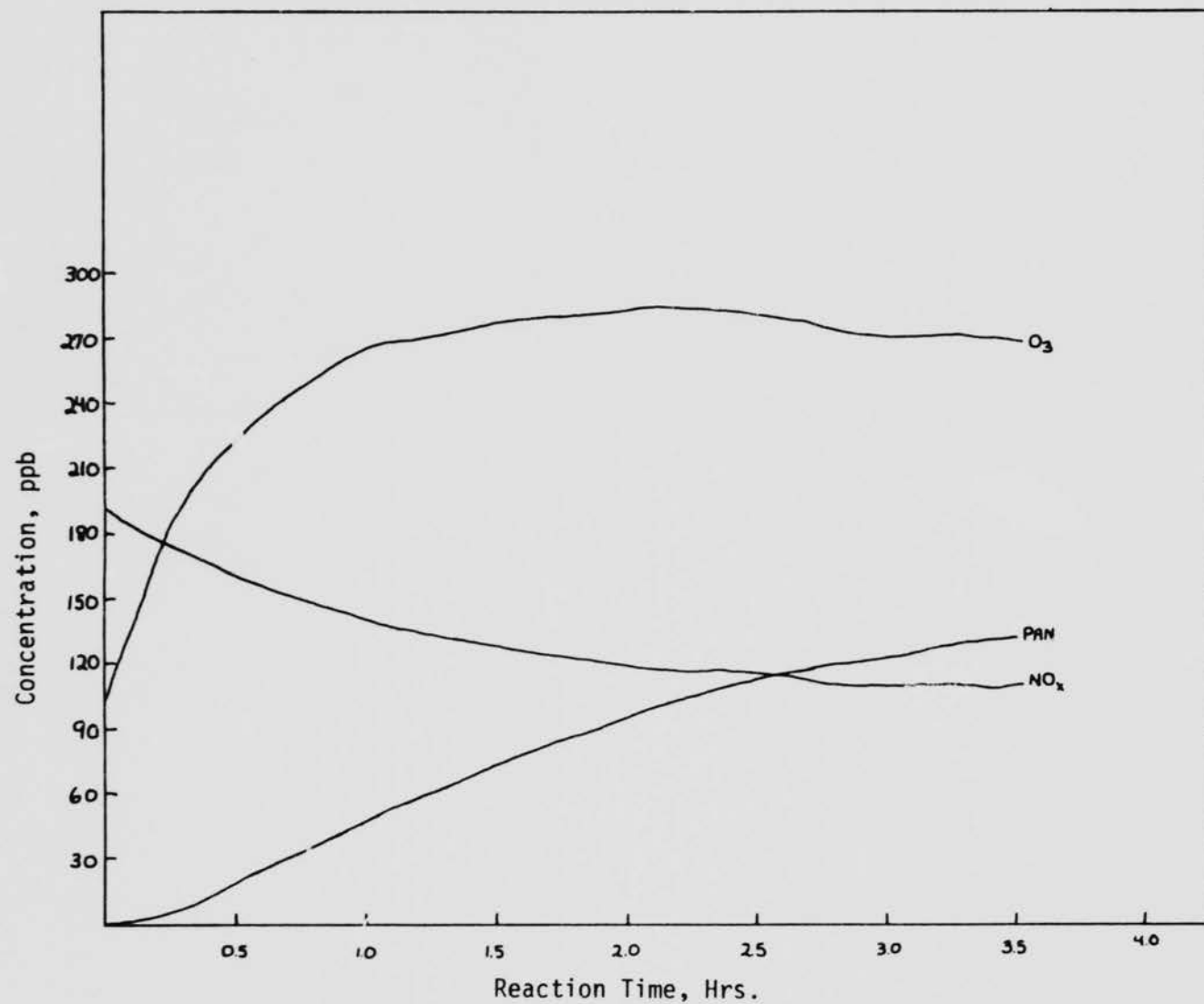
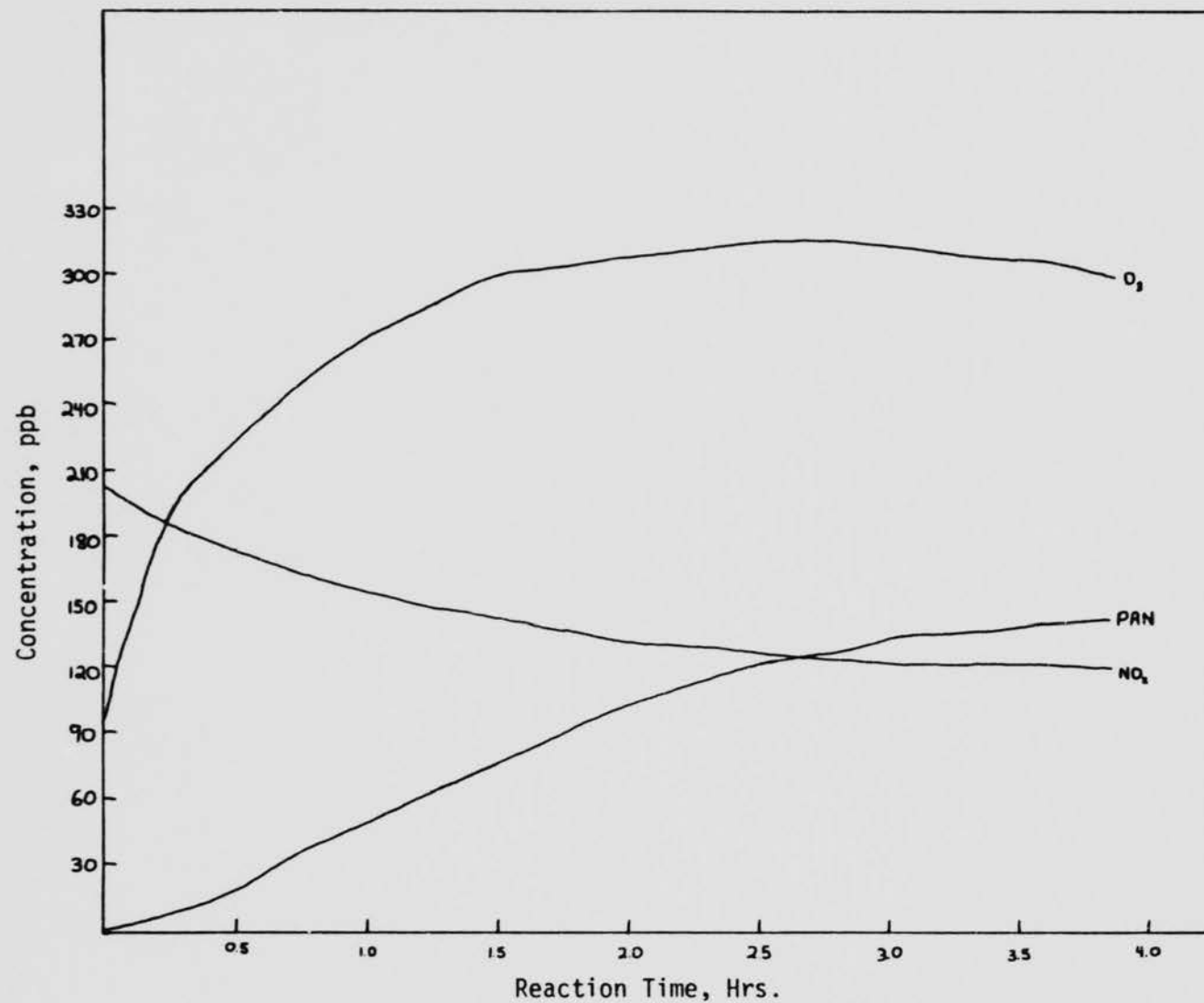FIGURE A8. EXPERIMENT 3 (Visual Distance 6 Miles @ O_3 Maximum)

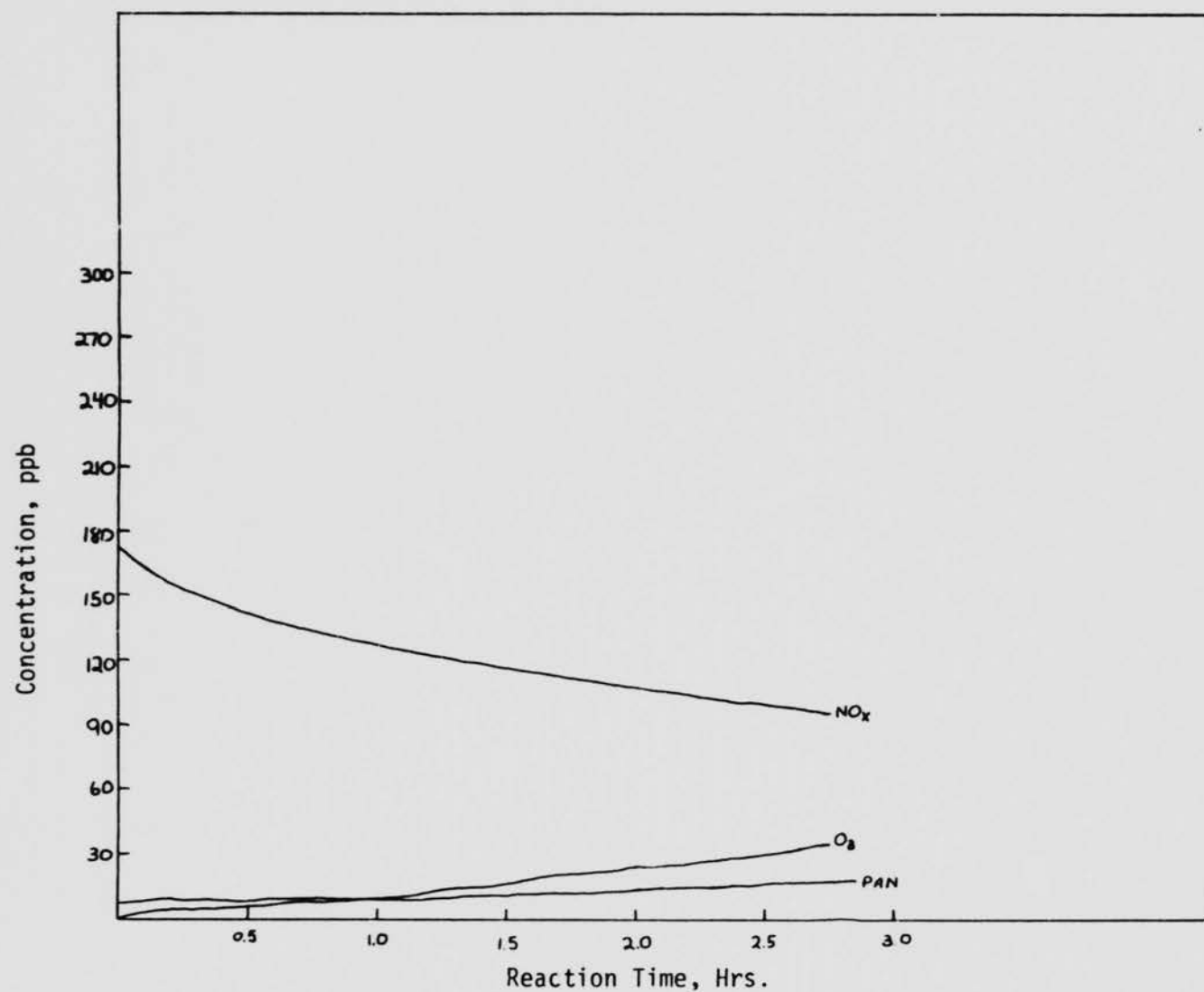FIGURE A9.   EXPERIMENT 4 (Visual Distance 6 Miles @ O_3 Maximum)

FIGURE A10. EXPERIMENT 5 (Visual Distance <0.3 Miles @ O_3 Maximum)
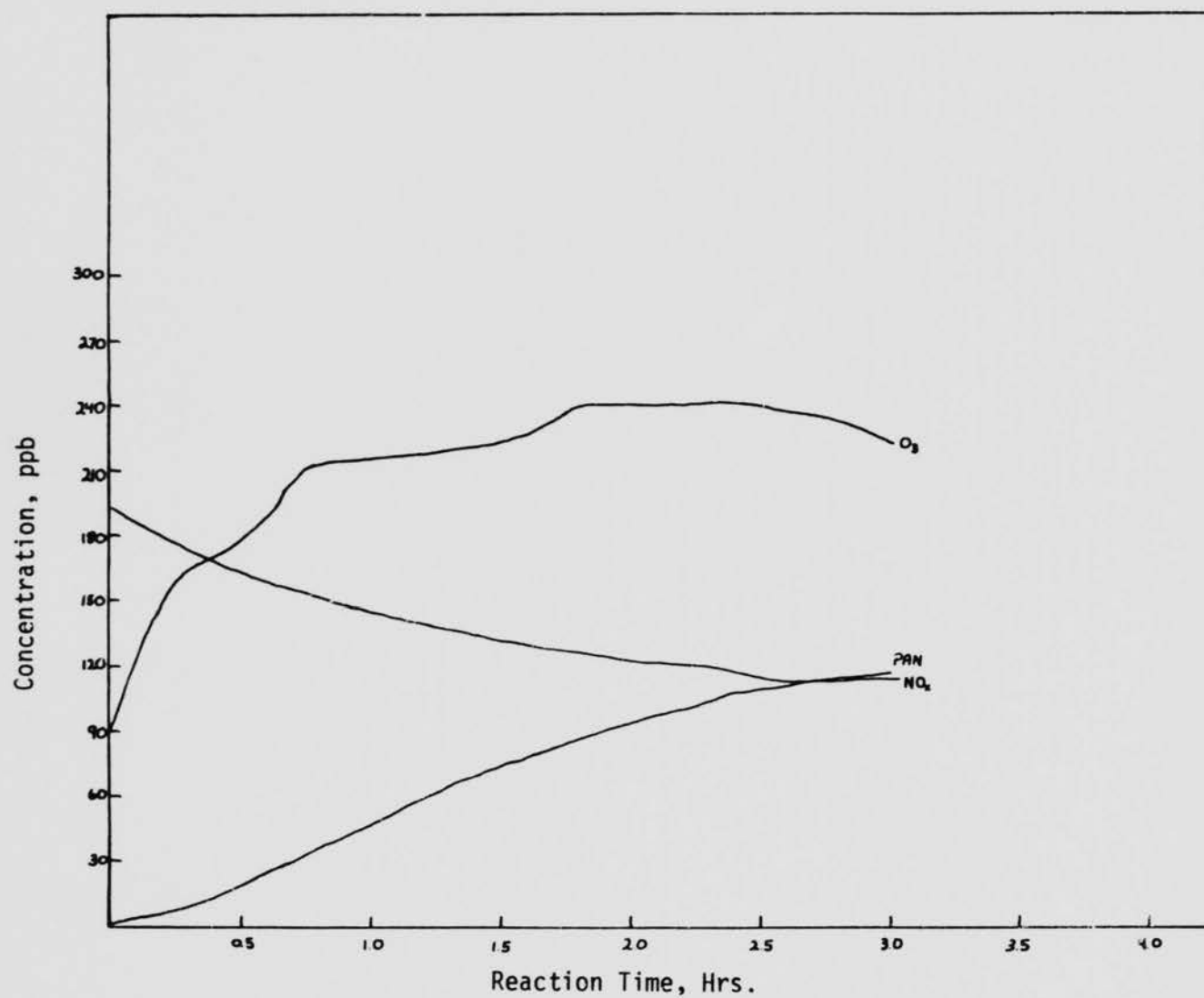
FIGURE A11.   EXPERIMENT 6 (Visual Distance 0.6 Miles @ O_3 Maximum)

TABLE A1. DATA FROM ASAS PARTICLE ANALYZER

Experiment No./ Irradiation Time	Particle Concentration (No./cm³)	Percentage Distribution According to Particle Size (Diameter = μm)										
		0.10	0.11	0.13	0.17	0.22	0.28	0.38	0.50	0.66	0.92	2.04
Experiment 3												
2.68 hrs	11,068	2.7	6.0	15.2	56.0	16.7	3.2	0.1	--	--	--	--
2.93 hrs	9,599	2.6	5.5	14.9	55.5	17.3	4.0	0.3	--	--	--	--
3.02 hrs	9,794	2.5	5.4	14.5	55.5	17.5	4.5	0.1	--	--	--	--
Experiment 4												
0.20 hrs	7,141	17.7	29.1	37.8	14.6	0.2	0.1	0.5	--	--	--	--
0.52 hrs	10,902	8.3	10.6	23.1	55.5	1.7	0.4	0.5	--	--	--	--
1.10 hrs	12,044	4.8	8.2	16.7	60.7	8.5	0.8	0.3	--	--	--	--
2.05 hrs	9,530	1.7	3.6	10.7	55.1	22.4	6.2	0.3	--	--	--	--
Experiment 5												
0.92 hrs	31,547	0.3	0.6	1.9	28.1	22.5	31.5	14.7	0.3	--	--	--
2.80 hrs	23,604	0.1	0.1	0.6	11.5	12.7	37.6	34.6	2.5	0.2	--	--
Experiment 6												
Chamber background	21	0.0	0.0	1.4	18.9	28.0	35.1	16.6	--	--	--	--
-0.10 hrs	4,830	1.9	2.7	5.0	20.3	16.7	23.8	22.0	6.4	2.2	--	--
0.82 hrs	11,738	1.3	2.0	4.6	21.0	16.0	21.5	21.1	6.8	2.0	--	--
1.53 hrs	12,263	0.8	1.4	3.3	20.4	18.1	24.9	21.4	6.6	2.4	--	--
2.43 hrs	12,157	0.5	0.8	2.0	16.2	16.2	26.8	28.2	6.8	1.7	--	--
3.05 hrs	10,769	0.5	0.8	2.0	17.1	17.4	28.5	23.0	7.0	2.9	--	--

TABLE A2.   ESTIMATE OF AMMONIUM SULFATE LOADING IN EXPERIMENT 6

(Particles/cc)	(Fraction) x	$((NH_4)_2SO_4$ Density) x	(Particle Volume-cm^3) =	Mass Concentration (g/cc)
(4830)	(.019)	1.8 gm/cc	5.2×10^{-16}	<1
	(.027)		7.0×10^{-16}	<1
	(.050)		1.2×10^{-15}	<1
	(.203)		2.6×10^{-15}	5
	(.167)		5.6×10^{-15}	8
	(.238)		1.2×10^{-14}	25
	(.220)		2.9×10^{-14}	55
	(.064)		6.6×10^{-14}	37
	(.022)		1.5×10^{-13}	29
	--		4.1×10^{-13}	0
(4830)	--		4.5×10^{-12}	0

Total = ~160 g/cc
or
160 µg/m³

NA-E-24

Drafte Addendum No.1.

RECEIVED

APR 1 5 1985

P. B. DUFF

April 15, 1985

Mr. Paul Duff
Olin Corporation
120 Long Ridge Road
Stamford, Connecticut 06904

Dear Paul:

Enclosed is a brief addendum to our Fate of TDI Phase II Report. As
agreed to by phone we conducted additional experiments designed to
distinguish between direct photolysis of TDI and free radical attack on
TDI. Likewise two DABCO/TDI experiments were carried out using equal
molar amounts of each compound. We utilized the HPLC/impinger technique
and MDA analyzer to monitor TDI loss during all experiments. However,
due to cost restraints we did not operate the O_3, PAN, NO_x, individual
hydrocarbon species, aerosol and toluene diamine monitoring
instrumentation.

Best Regards,

Mike

Mike Holdren
Principal Research Scientist
Physico-Chemical Systems Section

MH:sb

Enc.

ADDENDUM TO FATE OF TDI PHASE II REPORT

In an effort to identify the dominant chemical or physical processes which control toluene diisocyanate (TDI) lifetime and fate in the atmosphere, a series of six experiments was recently carried out with Battelle's 17 m^3 environmental chamber. An assessment of the following processes was made:

- TDI photolytic decomposition
- Reaction of TDI with photochemically induced pollutants (e.g., O_3, OH radicals)
- TDI reaction with ammonia
- TDI reaction with triethylene diamine (DABCO)
- TDI adsorption on ammonium sulphate particles.

Briefly, the experimental results indicated that the irradiation of TDI in "clean air" produced an increased loss rate over that observed in clean air in the dark. The use of highly polluted air did not appreciably enhance the rate of TDI disappearance compared to the clean air irradiation experiment. Experiments involving the addition of NH_3 and $(NH_4)_2SO_4$ aerosol also did not show significantly higher TDI loss rates. However, the addition of 2 ppm triethylene diamine, which is often coemitted with TDI, did appreciably accelerate the TDI loss rate.

In order to further investigate the role of photolysis in affecting TDI decomposition (i.e., TDI/clean air irradiation experiment), two additional experiments were conducted. TDI reaction with triethylene diamine using lower DABCO concentration was also examined. These additional experiments are listed in Table 1. Experiment 7 was carried out to provide a baseline for comparing with earlier Phase 2 results. Experiment 8 was designed to determine if the enhanced TDI loss rate observed in experiment 2 was due to direct photolysis or to reaction with radicals generated by photolysis of trace chamber contaminants. A radical scavenger, nitric oxide, was injected to suppress the effect of radical reactions so that direct photolysis of TDI could be distinguished from free radical attack on TDI. In experiments 9 and 10 equal molar amounts of TDI and DABCO were included,

TABLE 1. MATRIX OF ADDITIONAL CHAMBER EXPERIMENTS
FOR TDI PROGRAM[a]

Experiment No.	Light Conditions	Chamber Contents (@ 60% RH, 28°C)
7	Dark	Clean air 0.2 ppm TD-80
8	Light	Clean air 0.2 ppm TD-80 4 ppm NO (radical scavenger)
9	Dark	Clean air 0.2 ppm NO_2 4.0 ppmC (HC-mix) 0.2 ppm TD-80 0.1 ppm O_3 0.2 ppm triethylene diamine (DABCO)
10	Light	(above species after 1.5 hrs of reaction in dark)

(a) Chamber dilution was determined during each experiment by following the disappearance of injected SF_6 (6 ppb) using gas chromatography-electron capture detection.

along with a surrogate urban mixture, both in the dark and under irradiated conditions. These experiments provided additional data to supplement the results from an earlier experiment in which DABCO/TDI concentration ratio was 10.

The results of the four additional experiments, along with the original six runs, are shown in Table 2. For comparison purposes the loss rates have been corrected for chamber dilution and physical loss of TDI on the chamber surfaces. Average loss rate values shown in the table were determined from the HPLC/impinger technique and the continuous MDA analyzer. In reviewing the data from experiments 1, 2, 7, and 8, it is clear that free radicals, and not direct photolysis, are responsible for TDI removal in the irradiation experiments. In experiment 8, no significant increase in TDI loss was observed when compared with the results from the unirradiated baseline experiment (run 7). We interpret this to mean that the radical scavenger suppressed the effect of radical reactions, and that direct photolysis of TDI is not a significant atmospheric removal process. These results further allow us to conclude that the reaction of TDI with free radicals is a significant chemical process in controlling the lifetime and fate of TDI in the atmosphere.

The DABCO/TDI experiments show the following. At equal molar concentrations (0.2 ppm), no significant reaction between TDI and DABCO occurred in the dark (experiment 9). After 1.5 hrs of reaction in the dark, the chamber contents from experiment 9 were irradiated (experiment 10) and an enhanced TDI loss rate of 20%/hr over baseline was observed. A similar loss rate of 21%/hr was also found during irradiation experiment 3 in which DABCO was not present. These results suggest that the observed loss rate in experiment 10 is primarily due to TDI reaction with radicals generated photochemically from ambient air pollutants. Although reaction between TDI and DABCO is occurring (either in the gas phase or heterogeneously) as evidenced by experiment 5, the data are insufficient to determine whether atmospheric DABCO/TDI reactions are important when compared to TDI/radical reactions.

TABLE 2. SUMMARY OF TDI LOSS RATES DURING CHAMBER EXPERIMENTS
AFTER CORRECTING FOR CHAMBER DILUTION AND
BACKGROUND EFFECTS (Experiments 1 and 7)

Experiment No. and Conditions	MCA		Average TDI Loss[a] (percent/hr)
1 (Clean Air/No Irradiation)	15	15	0
2 (Clean Air/Irradiation)	40	32	21
3 (Surrogate Urban Mixture/Irradiation)	32	39	21
4 (Surrogate Urban Mixture Plus 0.5 ppm Ammonia/Irradiation)	34	31	18
5 (Surrogate Urban Mixture Plus 2.0 ppm DABCO/Irradiation)	96	102	84
6 (Surrogate Urban Mixture Plus 100 $\mu g/m^3$ Ammonium Sulfate/Irradiation)	41	33	25
7 (Clean Air/No Irradiation)	9	51	0
8 (Clean Air Plus 4 ppm NO/Irradiation)	4?	3?	3
9 (Surrogate Urban Mixture Plus 0.2 ppm DABCO/No Irradiation)	35	36	1
10 (Surrogate Urban Mixture Plus 0.2 ppm DABCO/Irradiation)	57	52	20

(a) Values determined by averaging data from HPLC/impinger technique and continuous MDA analyzer.

NA-E-24

Draft Addendum no. 2.

❋ Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201-2693
Telephone (614) 424-6424
Telex 24-5454

July 15, 1985

Mr. Paul Duff
Olin Corporation
120 Long Ridge Road
Stamford, Connecticut 06904

Dear Paul:

The purpose of this letter is to elaborate on the additional experiments we recently conducted with TDI, to present the data in the tabular format you requested, and to clarify the definition of lifetime and the units of the TDI rate constant.

In all of our reports we have presented TDI loss data in terms of a first order rate constant, k, with units of inverse time. For convenience, we have expressed k in reciprocal hour units (hr^{-1}), although other units of time could be used. We have used the term "lifetime" to mean the conversion or reaction lifetime, that is, the time it takes the reaction to reduce the TDI concentration to 1/e of its original value. In mathematical terms:

$$kt = \ln \frac{[TDI]_i}{[TDI]_t} \ .$$

$$\underline{When} \ \frac{[TDI]_i}{[TDI]_t} = e = 2.718$$

then $kt = 1$

and $t_{(lifetime)} = 1/k \ .$

In this formulation, k is the TDI loss rate constant (or loss rate for short), t is reaction time, and $[TDI]_i$ and $[TDI]_t$ represent the initial concentration and the concentration at time t. If the condition is met that $\frac{[TDI]_i}{[TDI]_t} = e$, then t is defined as the lifetime, and is computed

simply as 1/k. Another term which is sometimes used is half-life, which is calculated from

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \ .$$

When the rate constant is in units of hr^{-1}, the lifetime or half-life will be expressed as hours. In practical terms, the lifetime is the time it takes to reduce the initial concentration to $1/e$, or 0.367 of its original concentration.

Most of the Phase II data were provided in our Final Report dated February 5, 1985. Four additional experiments were run at your request and were summarized in our letter of April 15, 1985. Four more experiments have now been run and are included with this letter. The conditions of all the Phase II experiments are summarized in Table 1. The results of the experiments are shown in the format you requested in Table 2. Experiments 7-10 were run without the Teflon liner in the chamber. The liner was removed due to contamination after Run 6, at which time we believed the Phase II experiments were complete. Your concern over the effects of the aluminum chamber surface on the results of Experiments 7-10 prompted us to conduct experiments 11-14 at our own expense. Experiments 1-10 have been discussed in the earlier report and letter. Experiment 11 was carried out to recheck the baseline wall loss rate, which was in excellent agreement with the baseline rate of Experiment 7. Experiments 12 and 13 were carried out to determine whether the different chamber surface affects the TDI loss rate other than by increasing the baseline wall loss rate. These two experiments duplicate Experiment 5, with 2 ppm DABCO. The two experiments yielded higher gross TDI loss rates than Experiment 5, as expected due to the higher baseline wall loss rate, but the net loss rates (last column of Table 2) bracket the rate observed in Experiment 5. The average of the net loss rates for the two experiments is in excellent agreement with the Run 5 net loss rates, and the rates from the individual experiments are within 2 standard deviations of the Run 5 rate (see earlier report dated September 26, 1983 for estimate of standard deviation of chamber wall loss rates). Nevertheless, the variation in the rates from Experiments 12 and 13 is greater than we've experienced for TDI experiments, so we investigated potential causes by varying the order of addition of reagents in Experiment 13 (i.e. TDI before DABCO, rather than loading DABCO first). As seen in Table 2, the net rate was even higher, suggesting that very subtle differences in experimental conditions could result in large variations in TDI removal rate for such complex experiments. The experiment is complex in that it contains 17 organic compounds, nitric oxide, nitrogen dioxide, DABCO, and water vapor, and involves irradiation of this mixture. Each component of this mixture must be injected and mixed into the chamber, and different injection techniques are required for different components. If the main purpose of the experiments whose results are in question (i.e. Runs 9 and 10) is to elucidate the kinetics of the TDI-DABCO reaction, then it might be prudent to investigate this reaction without the complicating factors noted above, in an attempt to reduce the scatt   in the data.
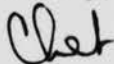
It is possible to check several of the experiments for consistency if we assume that TDI removal by free radical reaction and by reaction with DABCO are independent processes. In this case, the removal of TDI in Experiment 5 is the sum of the two processes, and we know from Experiment 3 that the free radical process contributes a removal rate of about 0.21 hr^{-1}. Therefore, the DABCO reaction is contributing about 0.63 hr^{-1} to the experiment removal rate (i.e. $0.84-0.21 = 0.63$). Experiment 10, with only one tenth the DABCO, might be expected to show a total rate made up of 0.06 hr^{-1} from the DABCO reaction and 0.21 hr^{-1} from the free radical reaction, for a total loss rate of 0.27 hr^{-1}. The actual rate measured for experiment 10 was 0.20 hr^{-1}. On the other hand, Experiment 9 indicates that, in the absence of the free radical mechanism (i.e. in the dark), 0.2 ppm DABCO contributes 0.01 hr^{-1} to the TDI loss rate, suggesting that the total removal rate for an experiment with both radicals and .2 ppm DABCO would be 0.22 hr^{-1}. Again, this value can be compared to the measured rate of 0.20 hr^{-1} for experiment 10. If an uncertainty of $\pm$ 15 percent is associated with these removal rates (see earlier report for this estimate), then the experiments demonstrate reasonable consistency.

Finally, I've come across an estimate of the rate constant for reaction of TDI with hydroxyl radical.* This value of 1.5×10^4 ppm^{-1} min^{-1}, when combined with the average hydroxyl radical concentration in our photolysis experiments ($\sim 2 \times 10^{-7}$ ppm) yield a first order TDI loss rate of 0.18 hr^{-1}, which is quite close to the 0.21 hr^{-1} loss rate observed for the experiment in which free radical processes were responsible for TDI removal (i.e. Experiment 3). This rate constant estimate can be used, together with the atmospheric hydroxyl concentration for a given situation, to calculate a TDI lifetime.

I hope this information proves to be useful to you. Incidentally, I've enclosed a hand-drawn graph which you might want to modify for your paper.

Sincerely,

Chester W. Spicer
Research Leader
Physico-Chemical Systems Section

CWS:mar

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* EPA Report EPA-600/3-84-082 (1984).

TABLE 1. SUMMARY OF PHASE II EXPERIMENTS

Experiment No.	Urban Mix	Irradiation	DABCO	Other Species	Comment
1	No	No	No	--	Baseline Wall Loss Rate
2	No	Yes	No	--	Clean Air Irradiation
3	Yes	Yes	No	--	
4	Yes	Yes	No	.5 ppm NH_3	
5	Yes	Yes	2 ppm	--	
6	Yes	Yes	No	100 $\mu g/m^3$ $(NH_4)_2 SO_4$	
7	No	No	No	--	Baseline Wall Loss Rate
8	No	Yes	No	4 ppm NO	Radical Suppression
9	Yes	No	.2 ppm	--	Dark Reaction
10	Yes	Yes	.2 ppm	--	
11	No	No	No	--	Baseline Wall Loss Rate
12	Yes	Yes	2 ppm	--	Repeat Run 5
13	Yes	Yes	2 ppm	--	Repeat Run 5
14	Yes	Yes	2 ppm	--	Repeat 13 With Reversed Order of Reagent Addition

TABLE 2. SUMMARY OF TDI DECAY RATES FOR PHASE II EXPERIMENTS

Experiment No.	TDI Removal Rate-MDA, hr^{-1}	TDI Removal Rate-Impinger, hr^{-1}	Avg. TDI Removal Rate, hr^{-1}	Net Loss Rate (TDI Removal Rate Minus Wall Loss Rate), hr^{-1}
1	.15	.15	.15	0
2	.40	.32	.36	.21
3	.32	.39	.36	.21
4	.34	.31	.33	.18
5	.96	1.02	.99	.84
6	.41	.38	.40	.25
7	.39	.31	.35	0
8	.41	.35	.38	.03
9	.35	.36	.36	.01
10	.57	.52	.55	.20
11	.36	--	.36	0
12	.99	--	.99	.63
13	1.43	--	1.43	1.07
14	1.61	--	1.61	1.25

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Summary of Phase II Experiments

Experiment Number

2 — Clean Air Irradiation

3 — Surrogate Urban Air Irradiation
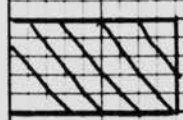
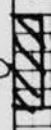4 — Urban Air Irradiation + 0.5 ppm NH3
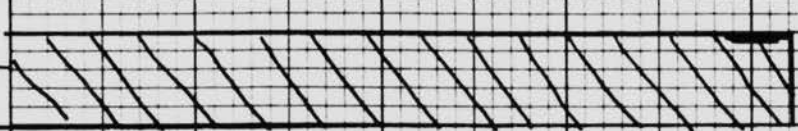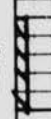
5 — Urban Air Irradiation + 2.0 ppm DABCO
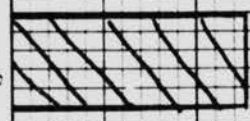
6 — Urban Air Irradiation + Particulate (NH4)2SO4

8 — Direct Photolysis (radicals supressed)

9 — Dark Reaction With Urban Air + 0.2 ppm DABCO

10 — Urban Air Irradiation + 0.2 ppm DABCO

0 .2 .4 .6 .8 1.0